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CHEMISTRY AND TECHNOLOGY OF THE PRODUCTION OF FIBER

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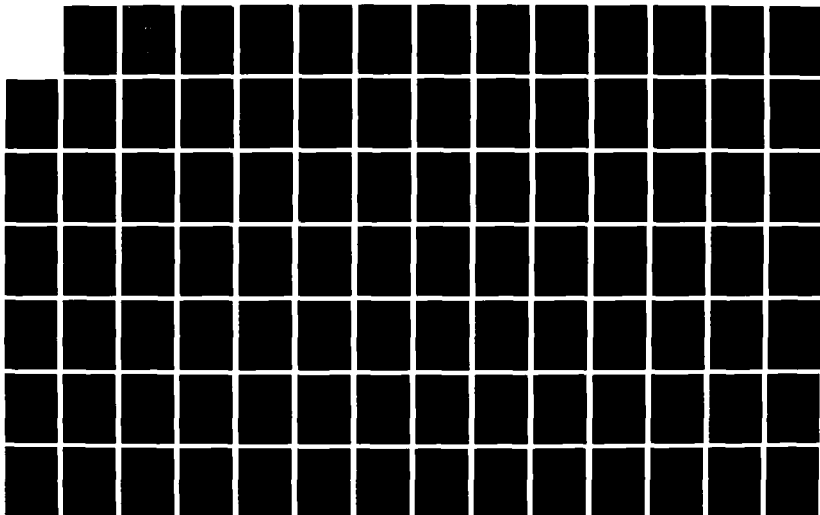
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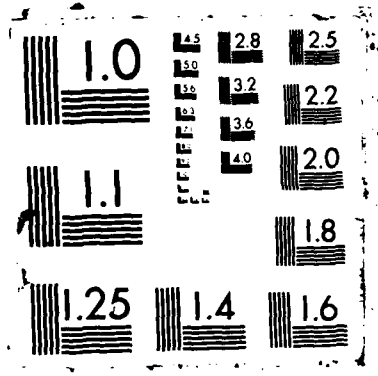
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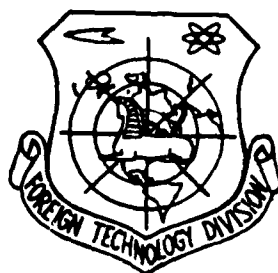
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CHEMISTRY AND TECHNOLOGY OF THE PRODUCTION OF FIBER NITRON

by

A.B. Pakshver, B.E. Heller



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In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

Page 51.

However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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TABLE OF CONTENTS

U.S. Board on Geographic Names Transliteration System	iv
Preface	3
Chapter 1. Short Survey of the Development of the Production of Fiber on the Basis of Polymers and Copolymers of Acrylonitrile	6
Chapter 2. Obtaining and Properties of Acrylonitrile	12
Chapter 3. Polyacrylonitrile as Raw Material for the Production of Intro-New Fiber	33
Chapter 4. Preparation of the Spinning Solution	86
Chapter 5. Spinning	116
Chapter 6. Finishing	153
Chapter 7. Dyeing	173
Chapter 8. Copolymers Fiber of Acrylonitrile with the Vinyl Monomers or From the Mixtures of Polymers	193
Chapter 9. Textile Properties of a Pan-Fiber	200
Chapter 10. Regeneration of Chemicals	215
Appendix 1. The Rate of Copolymerization	224
References	230
The Solvency of Some Organic Compounds with Respect to Polyacrylonitrile	231

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѐ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian English

rot curl
lg log

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CHEMISTRY AND TECHNOLOGY OF THE PRODUCTION OF FIBER NITRON.

A. B. Pakshver, S. G. Heller.

Page 2.

In pamphlet basic information about production of polymers and copolymers of acrylonitrile and fibers of them is presented. In it experiment of the production of fibers of the type the nitron, accumulated in the chemical industry, for the first time is summarized.

Book is intended for technical-engineering workers of industry of synthetic fibers. It can also serve as textbook for the students of chemical and textile VUZ [Institute of Higher Education].

Page 3.

Preface.

Development of production of synthetic fibers, plastics and other synthetic materials, which will make it possible to create enormous additional resources/lifetimes of raw material, necessary for preparing consumer goods, is one of most important problems of chemical industry of Soviet Union.

Production of synthetic materials is developed at vigorous tempo in the entire world. Thus, in the latter/last decade (from 1950 through 1960) the world production of synthetic fibers increased with 1646 thousand t almost to 3 million t. These fibers have long ago ceased to be substitutes - the defective substitutes of natural raw material. At present they are the qualitatively new materials, whose application must contribute to the development of many branches of industry.

In plan/layout of development of national economy during the years 1959-1965, affirmed by XXI Congress of KPSS [КПСС - CPSU], significant attention is given to increase in production of different synthetic fibers. With a total increase in the production of chemical industry almost 3 times output of synthetic fibers increase/grow 4.0 times, including production/consumption of synthetic fibers of the type caprone, nitron, Lavsan [polyethylene terephthalate film, Soviet equivalent of Dacron], khlorin, Anid will be increased

12-13 times.

Among different forms of synthetic fibers of special interest are fibers, obtained from polymers of acrylonitrile, and also from its copolymers with different monomeric compounds. Being characterized by high heat- and light resistance, by good thermal insulation properties, by stability to the effect/action of rotting bacteria and by other important properties, fibers of this type are the new most valuable form of textile raw material, equivalent, and in a number of cases exceeding the virgin wool.

World production of fiber on basis of polymers and copolymers of acrylonitrile rapidly is increased. In 1955 its production/consumption exceeded 45 thousand t, in 1959 it was increased to 160 thousand t.

Page 4.

At present fiber from polymers and copolymers of acrylonitrile is produced in many countries. In the USA this fiber produce by the name Orlon (Camden), Acrilan (Decatur), Kreslan (Stanford), GDR Vol'krilon [transliterated] (Wolfen), Prelan (Premnitz), FRG PAN (Frankfurt am Main), Dolan (Donau), Redon (Gol'shteyn) [transliterated], Dralon (Dormagen); in France Krilor (Lyon) and in Sweden Takril etc.

Up to 1960 plants of polyacrylonitrile fiber had to be constructed in many countries. Thus, must be started to the

exploitation plant in England by the power of 4500 t, in Japan with the power of 13500 t, etc.

In our country in 1965 about 30 thousand t of polyacrylonitrile fibers of type nitron will be manufactured.

In this book, calculated in technical-engineering workers of chemical industry, basic information on production of polymers and copolymers of acrylonitrile and fibers of them is assembled. In this book the authors for the first time try to generalize experiment of the production of fiber of the type the nitron, accumulated in the chemical industry, and to introduce scientific and technical community to the position in this branch of production; however the book does not pretend to the completeness of the illumination of all touched upon in it questions.

Chapters 1-4, and also applications/appendices are written to B. I. Kabanov. Chapters 5-10 are written by A. B. Pakshver.

Authors are grateful to coworkers of branch VNIIV by T. M. Ivanova, A. A. Heller, V. I. Maximov and by T. M. Kazachkova for help, shown/rendered during writing of book.

Authors will be very grateful for all critical observations, made aiming at book.

Authors.

Page 5

Chapter 1.

SHORT SURVEY/COVERAGE OF THE DEVELOPMENT OF THE PRODUCTION OF FIBER ON THE BASIS OF POLYMERS AND COPOLYMERS OF ACRYLONITRILE.

Unsaturated compounds of ethylene series/number have long ago attracted attention of chemists. In 1843 Redtenbacher (see [1]), studying the properties of unsaturated compounds, it for the first time synthesized acrylic acid; it were studied properties of some of its derivatives, including nitrile of this acid. However, industry at that time did not perceive the sharp/acute demand for the synthesis of new technical materials; whereas scientists were little interested in the substances, whose molecules were capable of the self-sealing (polymerization), and this discovery/opening remained that not noticed even by many organic chemists.

Investigations, carried out in latter/last quarter of past century in different countries, showed that acrylic acid $\text{CH}_2=\text{CHCOOH}$, its alkaline salts, amide, acid chloride, and also other derivatives can form highly polymeric products.

In 1894 French chemist Muro [2] for the first time obtained from acrylonitrile polymer, which is solid powder-like product, not dissolved in common organic solvents and which is only slightly softened at temperature, close to temperature of his decomposition.

In connection with this, in contrast to other numerous derivatives of acrylic acid, the easily polymerizing with the formation products, which could be used in the technology, acrylonitrile for a long time did not find industrial application.

In 1931 Carothers and its coworkers developed method of obtaining synthetic latexes - colloidal systems, which consist of polymer, dispersed in water [3]. As a result of developing the methods of the latex polymerization of butadiene and in particular his copolymerization with acrylonitrile in 1940 they began to produce on the industrial scales the new form of synthetic rubber - acrylonitrile rubber, which contains from 15 to 55% of acrylonitrile links. Articles made of this natural rubber are characterized by high resistance to the abrasion, heat- and by light resistance, by stability to many organic solvents and oils; they are resisted well aging and possess many other valuable properties.

Page 6.

Production of acrylonitrile, in view of its utilization for obtaining synthetic rubber, considerably was expanded in USA and Germany during years of Second World War. Work on the analysis of other products of polymerization and copolymerization of acrylonitrile simultaneously was conducted. The development of the methods of transforming this thermo- and light resistant polymer into the fiber was of great interest.

Under normal conditions polyacrylonitrile is not melted without decomposition; therefore synthetic fiber could be obtained from it only by solution spinning.

However, polyacrylonitrile is not dissolved in common organic solvents. The difficulties of the treatment/processing polyacrylonitrile into the fiber usually were explained by the presence of the cross chemical bonds between the macromolecules. It is here appropriate to note that the analogous hypothesis was advanced also with respect to polyvinyl chloride.

Both in the first and in second case this hypothesis proved to be erroneous. The theory, developed by V. A. Kargin and by Z. A. Rogovivin [4, 5], and also by Marvel [6] about the effect of intermolecular interaction in the polymers on their solubility in the polar solvents, it served as basis for the searches for the polar organic solvents, capable of tearing molecular bonds in polyacrylonitrile and of solvating macromolecules, converting them into the solution. For example, it was established that polyacrylonitrile is dissolved in the concentrated aqueous solution of thiocyanate sodium or calcium [7].

In 1942 almost simultaneously Rhine and Houtz [7, 8] as solvent of polyacrylonitrile proposed dimethyl formamide, which was jerk/impulse for development of production of polyacrylonitrile fiber.

For the first time polyacrylonitrile fiber was obtained in the form of silk on experimental installation in Weinsborough (USA) in 1944. Already the first tests of different articles made of the polyacrylonitrile fiber showed the effectiveness of the new form of textile raw material. Cloths from it were characterized by the ease/lightness, heat- and by light resistance, by wrinkle resistance, by the capacity to retain form by many other valuable properties.

In six years in Camden (USA) was started in exploitation first plant, which develops/depletes polyacrylonitrile silk and staple fiber by the name "Orlon" [8]. The production of polyacrylonitrile staple fiber in GDR and in the FRG almost is simultaneously organized.

However, already in first years of industrial production fibers on basis of acrylonitrile were revealed its two main disadvantages, which impede widespread implementation into industry of this new interesting form of textile raw material.

Page 7.

Fiber was badly/poorly stained with common dyes/pigments and possessed a certain brittleness. However, during the copolymerization of acrylonitrile with small number (5-10%) of different vinyl compounds (vinyl acetate, vinylpyridine, etc.) the properties of fiber were improved.

Comparative cheapness and accessibility of source material,

simplicity of polymerization and valuable properties of fiber conditioned stormy increase in production of polyacrylonitrile fiber in recent years. Cost/value 1 t of acrylonitrile on the world market in 1956 was to 30% lower than cost/value 1 t of terephthalic or adipic acid [9].

They form polyacrylonitrile fiber using dry and wet process. As the solvent the dimethyl formamide is used in essence; in insignificant quantities are used dimethylacetamide, α -pyrrolidone, ethylene carbonate, and also saturated solutions of some salts, mainly thiocyanate sodium.

With wet spinning are used water/aqueous precipitation baths or organic coagulants (glycerin, hexanetriol, spindle oil, kerosene, etc.).

Wet process of molding in organic precipitation baths, just as dry method, is used mainly for obtaining staple fiber with very high elementary number (more than 4500), and also in production of polyacrylonitrile silk.

Production of polyacrylonitrile fiber using dry method virtually nowhere is developed.

All new enterprises, which generate fiber on basis of polymers and copolymers of acrylonitrile, are intended for output of staple

fiber using wet process with application of water/aqueous precipitation baths.

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 9. Rayon a. Synthetic Text., 32, № 1, 71 (1950).
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Page 8.

Chapter 2.

OBTAINING AND PROPERTIES OF ACRYLONITRILE.

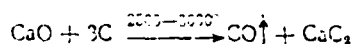
Acrylonitrile, or nitrile of acrylic acid, $\text{CH}_2=\text{CHCN}$ is produced on large/coarse industrial scale in many countries and is used for production of synthetic rubbers, fibers, plastic Masseys of other products of organic synthesis.

At present known several methods of synthesis of acrylonitrile. The greatest industrial value they acquired two methods of its obtaining: from ethylene and acetylene. In both cases the hydrocyanic acid is the second component, necessary for the synthesis of acrylonitrile.

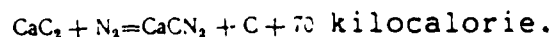
Obtaining hydrocyanic acid.

Of all used in industry methods of obtaining hydrogen cyanide oldest is its synthesis from cyanamide of calcium (Fig. 1).

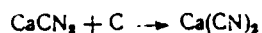
Lime and coke serve as source material. During alloying of unslaked lime with carbon/coal in electric furnace 1 carbide of calcium is formed. The process of the formation of carbide of calcium continues according to the following diagram:



Obtained carbide of calcium is loaded into the hermetically sealed batch furnaces 2, made from refractory material. In the center of furnace is established/installed electrical heating element. Carbide of calcium it is heated up to 800°, after which into the furnace nitrogen is supplied. As a result of the spontaneously proceeding reaction is formed gray powder-like product-cyanamide of calcium:



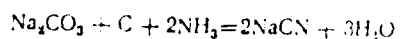
Alloying cyanamide of calcium with carbon/coal (coke) in electric furnace 3 is following stage of obtaining hydrogen cyanide; in this case is formed cyanide calcium:



Page 9.

It they treat by sulfuric acid in reactor 4 and is obtained damp/raw hydrocyanic acid, which then subjects to rectification in column 5.

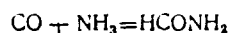
Somewhat more being expensive are method of obtaining hydrocyanic acid from sodium cyanide, which is generated during calcination of mixture of soda and carbon/coal in stream of ammonia with reaction:



In GDR is developed method of obtaining hydrocyanic acid from

carbon monoxide and ammonia; as intermediate product is formed formamide (Fig. 2).

In connection with this that under the effect of different admixtures/impurities of flow of reaction



it can be changed, is necessary thorough cleaning/decontamination of components of reaction, in particular carbon monoxide, from carbonate, gas, moisture and oxygen.

Process is accomplished/realized in vertical reactor, 1 where under pressure 150-200 atm. supply mixture of ammonia and methanol (playing role diluent); in mixture small quantity of methylete of sodium, which serves as catalyst, is contained.

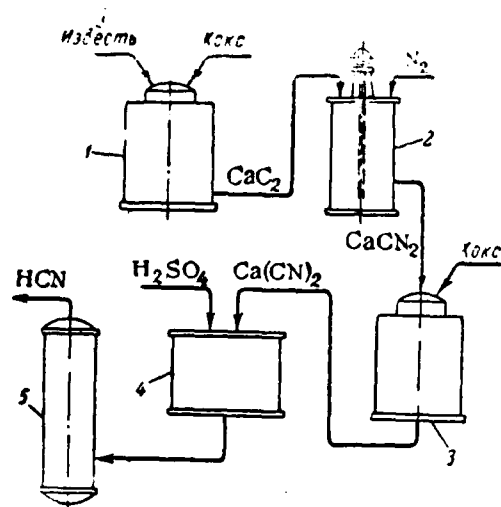


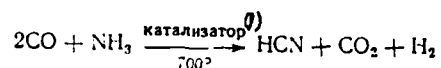
Fig. 1. Flow chart of obtaining hydrogen cyanide from cyanamide of calcium: 1 - electric furnace for obtaining carbide of calcium 2 - electric furnace for obtaining cyanamide of calcium; 3 - electric furnace for obtaining cyanide calcium; 4 - reactor for liberation/precipitation of hydrocyanic acid; 5 - rectifying column. Key: (1). Lime.

Page 10.

Simultaneously into the reactor carbon monoxide is supplied. Process proceeds at a temperature of approximately 100° . The unreacting gases return to the cycle after distillation column 2, in which occurs the first separation of the components of reaction. Damp/raw formamide for a second time is purified in vacuum-distillation column 3, then they supply into tube catalytic gas recombiner 4, where at 450° and pressure to 400 mm Hg it is split into the hydrocyanic acid, ammonia and water. Purified from ammonia in the columns of irrigation by 5 diluted aqueous solution of hydrocyanic acid comes for the

concentration into common filling columns 6. The emerging solution is to 35-40% hydrocyanic acid. The yield of hydrocyanic acid using this method reaches 75%, counting to ammonia.

In USA is used simplified method of synthesis of hydrocyanic acid from ammonia and carbon monoxide, which is taken in large excess. Reaction occurs in the presence of catalyst, most frequently aluminum, at a high temperature:



Key: (1). catalyst.

Process is accomplished/realized in continuous catalytic gas recombiners. The yield of hydrocyanic acid, counting to ammonia, composes 65% [1].

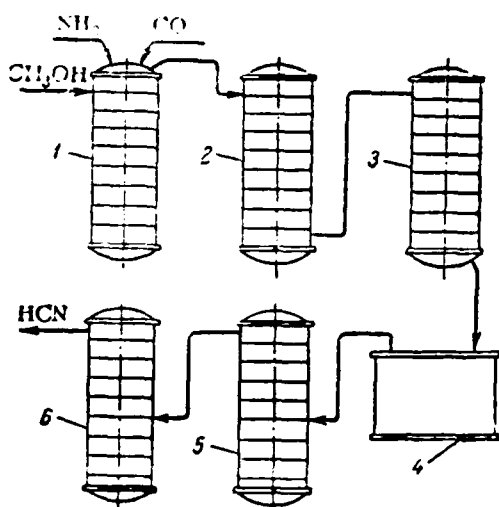
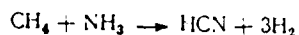


Fig. 2. Flow chart of obtaining hydrocyanic acid from formamide: 1 - vertical reactor for synthesis of formamide; 2 - distillation column; 3 - vacuum-distillation column; 4 - tube catalytic gas recombiner; 5 - column of irrigation; 6 - filling rectifying column.

Page 11.

Work on obtaining of hydrocyanic acid from natural gas via its catalytic amination under pressure [2] according to diagram



at present is conducted.

This method is, apparently, one of promising as a result of the cheapness of source material and simplicity of process itself.

Free hydrocyanic acid is very toxic light (sp. weight of approximately 0.7 g/cm^3) liquid with weak peculiar odor. Under the normal conditions it boils at 26° , and during the cooling it hardens

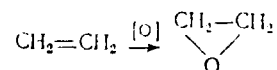
into the white crystalline mass, which is fused at -13° .

Obtaining acrylonitrile from ethylene.

In industry method of obtaining acrylonitrile from ethylene¹ it was for the first time applied in Germany [3]. Process consists of several stages.

FOOTNOTE¹. A basic quantity of ethylene is obtained with the pyrolysis of petroleum products. However, as the cheap source of ethylene can serve coke gas. At present it is used as the chemical raw materials only for obtaining hydrogen, which goes to the synthesis of ammonia. At the same time the content of ethylene in the coke gas is from 0.8 to 1.2% of vol. (about 2% of weight) or 0.375% of weight from reworked carbon/coal. During treatment/processing of tens of millions of tons of coking coals the powerful/thick production of ethylene can be organized. ENDFOOTNOTE.

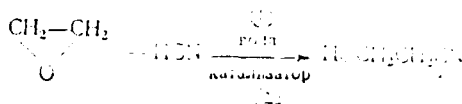
Ethylene oxide initially is obtained. For this purpose preliminarily purified ethylene is subjected to partial oxidation in special reactor 1 (Fig. 3). Reaction [4] occurs over the equation



Ethylene oxide is the liquid, which boils at $+12.5^{\circ}$.

From ethylene oxide is obtained ethylene cyanohydrin according to

following diagram:

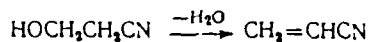


Key: (1). water. (2). catalyst.

This reaction is conducted in reactor 3. In it is poured the water, which contains 5-10 g/l NaOH and 30-40 g/l of dimethylamine and they simultaneously supply liquid oxide of ethylene and hydrocyanic acid. Reaction lasts more than 15 hours at 50-55°. After the end of reaction water they distill in the vacuum, and the remaining solution they neutralize by acetic acid on pH=5-6 and purify on filters 4. Usually ethylene cyanohydrin concentration in the obtained solution does not exceed 90%. Furthermore, are formed about 5% of glycol.

Page 12.

Dehydration $\text{HOCH}_2\text{CH}_2\text{CN}$ to acrylonitrile occurs in contact reactors (smashers) 5 at high temperature and in presence of catalyst. As the catalyst it is possible to use formate of calcium (in this case reaction is conducted [5] at 190-200°) or magnesium carbonate (reaction temperature it must reach 235°). Reaction occurs over the equation



Reaction products distill from smasher 5 into distillation column 6. From this column the mixture of the water vapors and acrylonitrile in the form of distillate is removed.

After condensation mixture is assembled into Florentine vessels 7, where as a result of limited solubility of acrylonitrile in water it occurs from lamination. They separate damp/raw acrylonitrile from the water and they subject to repeated distillation.

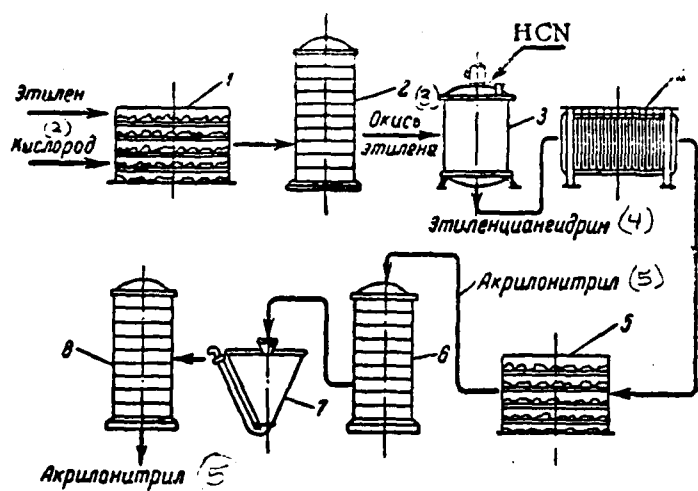


Fig. 3. Flow chart of obtaining acrylonitrile through ethylene cyanohydrin: 1 - reactor for synthesis of ethylene oxide; 2 - column of cleaning/decontamination of ethylene oxide; 3 - reactor for synthesis of ethylene cyanohydrin; 4 - filter; 5 - contact reactor-smasher; 6, 8 - distillation columns; 7 - Florentine vessel (separating agent).

Key: (1). Ethylene. (2). Oxygen. (3). Ethylene oxide. (4). Ethylene cyanohydrin. (5). Acrylonitrile.

Page 13.

Obtaining acrylonitrile from acetylene.

Direct synthesis of acrylonitrile from acetylene and hydrogen cyanide is very effective method. However, for its realization is required the thorough cleaning/decontamination of the components of reaction, in particular acetylene.

Acetylene on industrial scale usually is obtained from carbon/coal, lime and water. During alloying of carbon/coal with lime is formed carbide of calcium, from which under the effect on it of water is obtained acetylene. Process can be depicted as the following diagram:



Reaction is conducted in special gasifiers 1 (Fig. 4), which remind by construction/design of furnace for combusting sulfuric pyrite. Ground carbide of calcium interacts with the water vapors, supplied to a reactor-gasifier 1 through the special injectors. Temperature within the gasifier is maintained due to the heat, which separates in the presence of the reaction, in the limits from 98 to 105°.

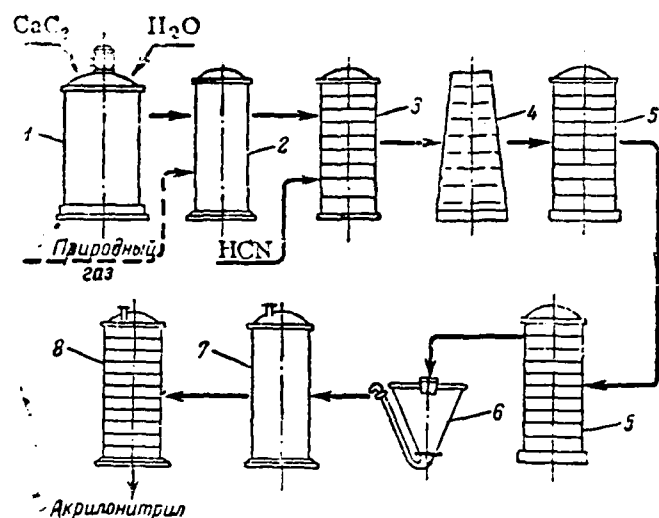


Fig. 4. Flow chart of direct synthesis of acrylonitrile: 1 - reactor-gasifier; 2 - column of irrigation; 3 - contact column-reactor; 4 - scrubber; 5 - filling columns; 6 - Florentine vessel; 7 - column of cleaning/decontamination; 8 - vacuum-rectification column.

Key: (1). Natural gas. (2). Acrylonitrile.

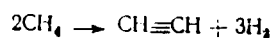
Page 14.

Acetylene obtained using this method possesses characteristic odor, which is conditioned on admixture/impurity of hydrogen compounds of sulfur and phosphorus. These pollution/contamination can be removed, passing the gas through the solution of mercurous chloride in the diluted hydrochloric acid. Acetylene is washed from the admixtures/impurities in the special columns of irrigation by 2.

According to another method acetylene is obtained by thermal decomposition of methane. At temperatures from 1600 to 3000° in the

presence of tungsten or carbon/coal during the extremely short time interval (0.0001 s.) the conversion of methane (to 65%) into acetylene [6] occurs. Significant propagation obtained also the cracking of methane to acetylene in the arc discharge in the conditions of reduced pressure [7].

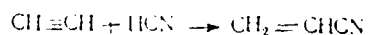
Processes in this case proceed according to following diagram:



Obtained acetylene virtually, besides undecomposed methane, no admixtures/impurities contains.

Thoroughly purified from impurities acetylene is supplied into contact column 3, where it reacts with here hydrocyanic acid [8] (to 1 mole HCN of 10 moles C_2H_2) entering. Reaction is conducted in the liquid (aqueous) phase in the presence of small quantities of mixture of hydrochloric acid and chloride salts of potassium, sodium, copper and cobalt.

Reaction gases continuously recirculate. The synthesis of acrylonitrile flows/occurs at 85-90° according to the diagram



The mixture of vapors of acrylonitrile and water is cooled and then they direct into scrubber 4. Hence emerges 7% aqueous solution of acrylonitrile, which contains different admixtures/impurities (HCN,

CH₃CHO, etc.). This solution subject distillation in filling columns 5, after which it enters the separation into Florentine vessels 6. Water/aqueous layer they direct to the recirculation, and the acrylonitrile layer, in which it is contained to 10% of water, they pump into the column of cleaning/decontamination 7 for the removal/distance of admixtures/impurities (hydrocyanic acid and acetaldehyde). Purified, but still containing water acrylonitrile they direct into a vacuum-rectification column 8, where the product finally is purified.

Acrylonitrile obtained using this method nevertheless contains small quantity of admixtures/impurities (vinylacetylene, methyl vinyl ketone, tracks of chloroprene, etc.), detrimentally influencing quality obtained polymers. From acetylene they purify methyl vinyl ketone, passing the gases through the solution of sodium hypochlorite at 30° during 15 min [9].

As a result of direct synthesis of acrylonitrile product, which contains about 2% of water, is obtained.

Page 15.

During comparison of method of obtaining acrylonitrile from ethylene with method of obtaining from acetylene it is evident that is more expedient as parent substance to use acetylene. The process of obtaining acrylonitrile of ethylene is more complex, since it consists of several stages. Furthermore, on its realization is

expended/consumed a large quantity of materials.

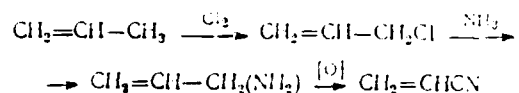
Process of obtaining acrylonitrile from acetylene it is possible to conduct into one stage by uninterrupted method, also, in this case to obtain sufficiently pure/clean product. However, a deficiency in this method consists in the need for spending a large quantity of electric energy on obtaining 1 t of acetylene from carbide of calcium it is approximately 12000 kWh, and to the synthesis 1 t of acetylene with the electrocracking of methane [10] more than 10000 kWh. Therefore acetylene generation must be developed mainly in the places with the cheap electric energy. This deficiency can be overcome by the application of a thermo-oxidizing cracking of methane.

At present acetylene method of obtaining acrylonitrile acquires high importance in connection with possibility of utilization of cheap electric energy of greatest hydroelectric power stations, constructed in Volga, Mangar and other rivers, and also because of discovery/opening of largest deposits of natural gas in North Caucasus, in Western Siberia and especially in Central Asia.

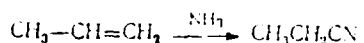
Obtaining acrylonitrile from propylene.

New method of synthesis of acrylonitrile with utilization as source material of propylene was recently proposed. In one of the patents it is indicated that acrylonitrile can be obtained by the selective chlorination of propylene to allyl chloride, which during

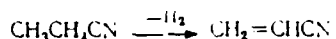
the processing/treatment by ammonia is converted into allylamine. In the presence of silver catalyst allylamine is oxidized to acrylonitrile [11]:



Is also of interest straight/direct amination of propylene at 350-425° under pressure to 210 atm(gage) in presence of nickel or cobalt catalyst:



As a result of this process is obtained mixture of nitriles, which contains more than 50% propionitrile. If mixture is passed above the catalyst (oxide of chromium) at 625°, then propionitrile is dehydrogenated to acrylonitrile [12]:



Page 16.

Presence of enormous resources/lifetimes of propylene in our country will make it possible, apparently, to use these methods of obtaining acrylonitrile.

Properties of acrylonitrile.

For obtaining polyacrylonitrile, suitable as raw material in production of fiber, very pure/clean acrylonitrile is necessary; quantity of all forms of admixtures/impurities in it, with exception of water, must comprise not more than 0.005%.

At room temperature and common pressure acrylonitrile is colorless liquid with peculiar odor. Its boiling temperature is equal to 77.3° ; freezing point - 83.6° ; dipole moment is equal to 3.88; weight at 20° is 0.8060 g/cm³; refractive index [13] $n_D^{20} = 1.2588$

Acrylonitrile is limitedly water-soluble. Are cited below the data (into % weight) about the solubility of acrylonitrile in the water and water in acrylonitrile at different temperatures [14]:

Temperature, by $^{\circ}\text{C}$... 0 20 40 60 80.

Liquid-water content in acrylonitrile, % weight. 2.1 3.1 4.8 7.6 11.0.

Content of acrylonitrile in water, % weight. 7.2 7.4 7.9 9.1 10.8.

Acrylonitrile with water forms azeotropic mixture, which contains 83% of acrylonitrile and which boils at 71° . Are given below some properties of acrylonitrile:

Heat capacity, cal/g·deg... 0.50.

Heat of vaporization, cal/mole ... 7.8.

Pressure of saturated vapor with 25°, mm Hg ... 108.

Temperature of spontaneous ignition, °C ... 481.

Maximum dangerously explosive concentration in air at 25°, % volume ... 3-17.

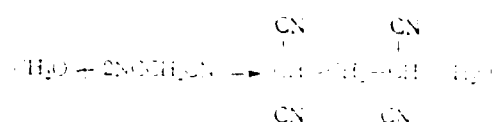
For preventing autopolymerization of acrylonitrile, which can occur under effect/action of light/world, into product are introduced different stabilizers: hydroquinone, anthracene, pyridine, amines [15] (for example, n-phenylenediamine in quantity 0.08% of weight). In the presence of stabilizers even during the heating up to 150° in the absence of oxygen does not occur the polymerization of acrylonitrile [16]. However, to obtain absolutely pure/clean acrylonitrile is difficult, since in the process of multistage washings and distillations it nevertheless partially is polymerized.

Page 17.

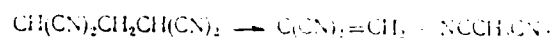
There is significant interest for synthesis of polymeric fiber-forming materials also in another nitrile derivative of ethylene - vinylidenecyanide $\text{CH}_2=\text{C}(\text{CN})_2$, which finds increasing use.

There are two industrial methods of obtaining vinylidenecyanide [17, 18].

First method is based on synthesis of 1,1,3,3-tetracyanopropane from formaldehyde and nitrile of malonic acid:



Generating tetracyanopropane cracks:

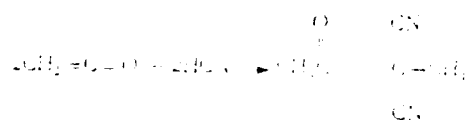


Cracking is conducted at 150-250° and residual pressure from 2 to 50 mm Hg.

The output/yield of vinylidenecyanide reaches 93%.

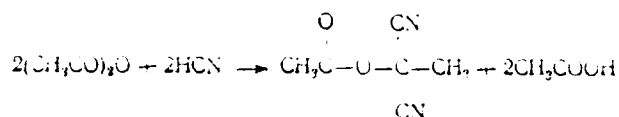
Second method of synthesis consists in pyrolysis of 1-acetoxy-1,1-dicyanoethane, which is generated as a result of reaction of ketene or acetic anhydride with HCN.

Reaction of ketene in HCN flows/occurs in vapor phase in presence of that activated Al_2O_3 at 300-400° and atmospheric pressure:



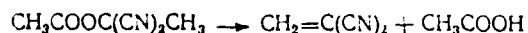
Maximum output/yield, counting on HCN, composes 40-45%.

If we apply acetic anhydride instead of ketene, then reaction occurs according to diagram:



This reaction is conducted in the liquid phase in the presence of tertiary amines at 40-60° and the atmospheric pressure. The output/yield of 1-acetoxy-1,1-dicyanoethane (counting to the acetic anhydride) composes 24%.

Conversion of 1-acetoxy-1,1-dicyanoethane into vinylidenecyanide is produced to Pyrolizome in vapor phase at pressure 2-50 mm Hg and to temperature of 600-650° in presence ZnCl_2 , the playing role catalyst:



Purified vinylidenecyanide is colorless transparent liquid, which boils at 153.5° and which freezes at -9.5°. With 2 mm Hg the boiling point of its is equal to 47°. Vinylidenecyanide is very toxic and causes strong epiphora. As the stabilizer of vinylidenecyanide the benzene is used. The temperature of its storage must not exceed 45°.

Page 18.

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Page 19.

Chapter 3.

POLYACRYLONITRILE AS RAW MATERIAL FOR THE PRODUCTION OF INTRO-NEW FIBER.

Polymerization of acrylonitrile.

In comparison with other vinyl compounds acrylonitrile is characterized by large polarity. Thus, the dipole moment of propylene is equal to 0.35, vinyl chloride - 1.44, and acrylonitrile - 3.88. By this, apparently, is explained its great tendency toward polymerization [1, 2]. Acrylonitrile extremely easily is polymerized under the effect of ~~γ~~-rays ([3, 4], X-rays [5], ultraviolet radiation [6], under the effect of the energetic electrons [7] and ultrasonic oscillations/vibrations [8]. For the initiation of polymerization reaction [9] were proposed to use also the rays/beams of the visible part of the spectrum when, in the polymerizable system, small quantities of fluorescein are present, or its haloid derivative.

Best conditions for course of polymerization of acrylonitrile are created during utilization of different chemical initiators - inorganic [10] and organic peroxides, and also other substances, which are easily decomposed into free radicals [11-14]. It is very convenient to use reduction-oxidation systems, for example the mixture

of the persulfate of potassium and bisulfite of sodium in acid medium [15, 16]. In practice in essence the initiated polymerization of acrylonitrile, which carries chain radical character, is used.

Theory of chain reactions, developed by N. N. Semenov [17] and other scientists, proved to be very fruitful. The application/appendix of this theory to the polymerization made it possible deeply to penetrate in the essence of process [18]. Entire accumulated at present experimental material on polymerization and copolymerization of acrylonitrile confirms the chain character of the mechanism of this reaction.

Methods of polymerization.

There are several methods of polymerization of acrylonitrile or its copolymerization with different vinyl compounds:

1. Mass polymerization.
2. Emulsion polymerization or suspension.
3. Polymerization of monomer, dissolved in water.

Page 20.

4. Solution polymerization with formation of concentrated solution of polymer ("varnish" method of polymerization).

Polymerization of acrylonitrile in block, which they conduct in the absence of solvent or diluents of monomer, is connected with great

difficulties, since it flows/occurs at a high speed. Process is accompanied by the liberation of a significant quantity of heat [19]; therefore regulating process becomes impossible, and reaction is usually completed by explosion. However, using different initiators, it is possible to sometimes obtain the soluble polymers. The concentrated solutions of such a polyacrylonitrile prove to be usually strongly structured [20]. The block copolymerization of acrylonitrile with different monomers [21] obtained greater application.

Insolubility in monomer of generatrix of polymer, which settles into precipitate, is special feature of process of block polymerization of acrylonitrile.

Emulsion polymerization or suspension, just as polymerization of monomer, dissolved inlet/introduction, is conducted in aqueous phase. These methods acquired the greatest industrial value, since while conducting of process in the aqueous medium polymerization reaction can be conducted at a velocity, which makes it possible to regulate temperature and to obtain the polymer of assigned molecular weight.

Usually is called emulsion polymerization process, during which initiating substances, soluble in monomer, but not soluble in dispersion medium, are used; suspension polymerization flows/occurs under the effect of initiators, dissolved in dispersion medium and not soluble in monomer.

Polymerization is either by common, periodic method or by uninterrupted, tower method in enamelled or steel reactors. With the periodic method the obtained suspension of polymer in the water is decanted to the filters, and apparatus is again filled with reaction mixture. With the tower method from the reactor the polymer continuously is selected/taken either in the form of thin stable emulsion - latex or in the form of suspension.

Fig. 5 gives fundamental flow chart of obtaining polymers or copolymers of acrylonitrile with uninterrupted method. In an autoclave-reactor 1, equipped with mixer, from special tank 2 continuously acts the reaction mixture, which consists of the water, emulsifier, the regulator of surface tension, regulator pH and initiators. From tank-measuring tanks 3 is metered acrylonitrile, and in the case of copolymerization and by the second of components. The suspension of polymer obtained as a result of reaction enters separating apparatus 4 for the distillation/removal of the unreacting monomers.

Page 21.

After condensation in the cooler of 5 pairs of monomers they enter the repeated distillation and return to the production process. The concentrated suspension of polymer they transmit with the aid of conveyer screw 6 to vacuum filters 7, and then into continuous dryer 8. The part of the polymer in the form of dust is taken away by air and is caught in cyclone-apparatuses.

With emulsion polymerization of acrylonitrile, used in USA, one should on 3.2 m³ of distilled water take 800 kg. of lauryl sulfate of sodium. As the initiator is used the redox system, which consists of 4 kg. of pure/clean ammonium persulfate [(NH₄)₂S₂O₈] and 1.82 kg. of metabisulfite of potassium (K₂S₂O₅). For the creation of the required acidity to the reaction mixture 0.1 of 1 n. of sulfuric acid are added. In obtaining of copolymers (for example, acrylonitrile-butadiene) emulsion method is basic.

Method of suspension polymerization of acrylonitrile received considerably more propagation. The polymer, used in the production of fiber Orlon, is obtained by slurry method with the utilization of redox system [22]. Relationship/ratio oxidizer (ammonium persulfate) and reducer (sulfur dioxide, the bisulfite of sodium) can be varied in the limits from 0.1 to 1. Initiator is recommended to introduce in a quantity from 0.1 to 4% of the weight of monomer.

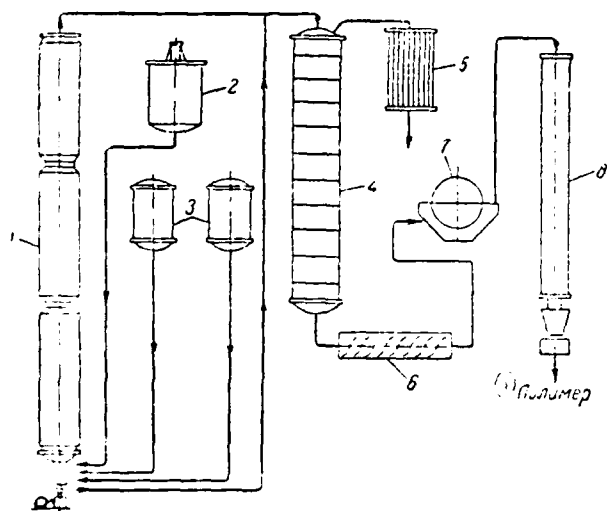


Fig. 5. Flow chart of obtaining of polymers and copolymers of acrylonitrile: 1 - continuous autoclave-reactor; 2 - tank for preparation of reaction SMSI; 3 - tank-measuring tanks of monomers; 4 - separating apparatus; 5 - capacitor/condenser; 6 - conveyer screw; 7 - vacuum filter; 8 - continuous dryer.

Key: (1). Polymer.

Page 22.

PH value of medium is maintained in the range from 2 to 5. The temperature of polymerization is equal to 29-49°; the duration of process 1.5-3 hour. The output/yield of polymer composes 80-85%. Molecular weight of the obtained polymer, depending on reaction conditions, can be regulated in the limits from 14000 to 225000. For reduction in the surface tension, and also for the stabilization of molecular weight into the reaction medium one should add mercaptans, polyhalide compounds, aldehydes, ketones, hydrazines, ethers/esters and other substances.

According to another version of method of latex polymerization, accepted in GDR, as initiator of process hydrogen peroxide is used. In this case the polymer is obtained sufficiently to pure/clean, and its solutions are filtered well. Polymerization is accomplished/realized as follows. In the autoclaves for the polymerization load 1000 pbw of water, 150 weight, h. of acrylonitrile even 12 weight. h. of perhydrol (33% the aqueous solution H_2O_2). They conduct process in the atmosphere of nitrogen during the

energetic mixing and temperature of 75°. Duration of polymerization 4-5 hour. For this time are polymerized about 80% of loaded acrylonitrile. A deeper flow of reaction is inadmissible, since the polydispersion of product in this case increases/grows. However, to obtain polymer with the reproducible properties by this method is very difficult.

At present polyacrylonitrile in essence is obtained by polymerization of monomer, dissolved in water. In this case also it is necessary to mix reaction mixture, but it is not so energetic as with the emulsion or suspension polymerization. For example, in the USA polyacrylonitrile is obtained with the aid of this method by following path of [23]. On 1000 l of the distilled water by 53 kg. of pure/clean acrylonitrile are taken. The initiating system consists of 1710 g of ammonium persulfate and 710 g of sodium metabisulfite. For the creation of the necessary pH value 29 g of 100%- sulfuric acid are added. They conduct polymerization in the atmosphere of nitrogen at 35°. The obtained polymer dries 16 hours. at 70°. The output/yield of product is equal to 92%.

GDR in obtaining of polymer for the fiber of Prelan are used the following regime/conditions of polymerization [24]. To 220 l of the purified water, which contains about 30% of methanol, 14.4 kg. of freshly distilled acrylonitrile during the intensive mixing pour. Then, continuing to mix, the catalyst, which is mixture of 144 cm³ of concentrated sulfuric acid, 17 g Fe(NH₄)(SO₄)₂, dissolved in 2 l of water, is added; 36 g K₂S₂O₈, dissolved also in 2 l of water, and 108

g $K_2S_2O_8$ of those dissolved in 3 l of water. After the introduction of all substances they stop mixer, and polymerization occurs spontaneously during 1-2 hour. Reaction occurs at 25-40°. Changing temperature, it is possible to obtain the polymers of different molecular weight - with larger molecular weight at a lower temperature and with smaller - with the higher.

Page 23.

The obtained suspension of polymer is supplied by diaphragm pump into the centrifuge, where catalyst is removed. Then they express polymer and they dry with 60-80%.

In Soviet Union is used so-called method of static polymerization of monomer in solution [25], which is accomplished/realized as follows. In the reactor to every 100 l of water are loaded by 7.0-7.4 kg. of acrylonitrile, 20-25 ml of sulfuric acid (ud weight 1.84), 75-80 g of the persulfate of potassium and 35-30 g of sodium hydrosulfite $Na_2S_2O_4$. Polymerization begins at 20°. After 70-80 min. the output/yield of polymer reaches 98%. They conduct process without the transferring, the heating or the special cooling. It is regulated only by composition of the starting material.

By this method polymer with sufficient reproducibility of basic properties (on polydispersion, viscosity/ductility/toughness of concentrated solutions, etc.) does not succeed in obtaining, and at present it is replaced by new, more advanced, controlled process.

It is very small literature data about continuous polymerization of acrylonitrile. Thus, are recommended [26] the conducting of continuous polymerization of the presence of redox initiator, who consists of Berthollet salt (0.377% from the weight of monomer) and sulfite of sodium (1.35%), with pH=3.0-3.5. They maintain the acidity of medium by the uninterrupted addition of sulfuric acid; its concentration must be 0.64% of the weight of monomer. It is desirable to conduct process in the atmosphere of nitrogen or carbon dioxide. Were proposed [27] to polymerize acrylonitrile in the presence of the initiating system persulfate-metabisulfite during the addition of sulfuric acid, and also in the atmosphere of nitrogen.

Recently [28] is described one of methods of continuous polymerization of acrylonitrile, which occurs in its 7.5% aqueous solution in presence of persulfate-metabisulfite initiating system. As the catalysts into the reaction mixture is introduced the acidity of reaction medium it is achieved not by discontinuous addition to the apparatus of sulfuric acid. Depending on the conditions of polymerization reaction lasts from 20 min. to 10 hour. Molecular weight of the obtained polymer, depending on the regime/conditions of polymerization, vary within the range of 77 500 to 174 000. For obtaining the polymer with molecular weight of about 100 000 are recommended to introduce into reaction mixture 1.5% $K_2S_2O_8$ and 0.5% $K_2S_2O_5$ from the weight of monomer, and also 0.047% of ferrous salt in the recount at $[Fe(NH_4)]^{+}$, and pH of medium to maintain in limits of

2.5- 3.0.

Page 24.

It is established that with an increase in the temperature of polymerization from 20 to 35° molecular weight of the obtained polymer virtually is not changed. With further increase in the temperature lower-molecular products are formed. The output/yield of polymer is satisfactory.

It is established that while conducting of continuous process of polymerization in presence of hydrogen peroxide output/yield of product does not exceed 20%, but molecular weight of polymer is comparatively low (44 200). Good results were obtained [28] during the application as the catalyst of sulfate of copper (0.09% of the weight of acrylonitrile) in the presence of persulfate-metabisulfite initiator. At a temperature of reaction of 40° output/yield of polymer reached 42%, its molecular weight was approximately 100 000.

Stability of physicochemical properties of obtained polymer is advantage of continuous process of polymerization over periodic mainly. At the same time during the continuous process of polymerization is required thorough preparation and cleaning/decontamination of the components of reaction, and also their accurate dosage.

There is significant interest in "varnish" method of

polymerization, whose essence consists in the fact that polymerization is conducted in solvent, which dissolves monomer, and polymer.

If with solution polymerization it was possible to obtain concentrated solution of polyacrylonitrile, which has necessary molecular weight, then after filtration of solution and its deairing it was possible to immediately form fiber. In this case the technology of obtaining fiber must considerably be simplified and it would be possible to eliminate the operations of landing, washing and drying of polymer, and also its dissolution.

It is known for [29] that acrylonitrile under the effect of redox initiator, who consists of hydroperoxide of cumol and triethanolamine, is capable to be polymerized of dimethyl formamide, which is solvent of polymer; however, with relationship/ratio of acrylonitrile and dimethyl formamide, equal to 1:7, polyacrylonitrile settles into precipitate. Therefore under such conditions to prepare the spinning solution by the polymerization of acrylonitrile in the solvent is not virtually possible. Furthermore, the obtained polymer has low molecular weight. This is explained by the fact that dimethyl formamide (DMF) analogous with the majority of other solvents acts as the carrier of chain [30].

Khun'yar [transliterated] and Gresset [31] it was possible to obtain spinnable solutions of polyacrylonitrile by polymerization, initiated by ultraviolet radiation, in system zinc chloride - calcium

chloride - water. As the catalyst ferric chloride was used. Optimal results were obtained during irradiation of mixture by ultraviolet radiation with the wavelength 334 mμ.

Page 25.

In this case trivalent iron most fully is reduced to the bivalent. Experiments showed that it is possible to regulate molecular weight of polymer by changing the quantity of ferric chloride.

Authors [31] proposed following regime/conditions of polymerization. To 1800 g of the solution, which consists of 35 g $ZnCl_2$, 20 g $CaCl_2$, and 45 g of water, added 200 g of acrylonitrile, 90 ml of that concentrated NCl_3 and 4.4 g $FeCl_3 \cdot 6H_2O$. In the avoidance of the formation of those branched to the mixture ethers/esters of thioglycolic acid added the regulator of reaction. The initial temperature of polymerization there were 50°. Irradiation was conducted for 1 hour of 50 min. By the quartz lamp of immersion of the type PRK-2. As a result of reaction acrylonitrile was converted to 70% into the polymer. The obtained solution had a viscosity of approximately 20 poise and was spun into the water at 10°. However, the quality of fiber proved to be low.

Was proposed also [32] to conduct polymerization of acrylonitrile in presence of oxidative-reductive initiators in aqueous 50% solution of thiocyanate salts. For regulating the polymerization 0.5-1.5% (from the weight of monomer) of itaconic acid sometimes are added.

In the solutions of thiocyanate salts generating polyacrylonitrile is capable to be dissolved.

Usually solution polymerization is conducted by continuous method, which provides obtaining uniform spinning solutions.

Polymerization of acrylonitrile in solution of nitrile of isobutyric acid at 60° with application as initiator of benzoyl peroxide [33] was investigated.

As early as 1946 it was discovered, that acrylonitrile was capable to be polymerized in solution DMF under the effect of boron trifluoride (BF₃). The experiments carried out by Kimball [34] on the polymerization of acrylonitrile in the solutions of dimethyl formamide, dimethylacetamide, N- methylpyrrolidone and in other solvents showed that it is possible to obtain polymers and copolymers of acrylonitrile, if we carry out the reaction at a temperature of higher than 100° in the presence of oxygen. At a polymerization during 18 hours in the atmosphere of pure nitrogen and a temperature of 100° only the minute quantity of polymer is formed. In the presence of oxygen the output/yield of polymer reaches 48%. As the initiators of the polymerization reaction, which takes place in these solvents, it is possible to also use AlCl₃, SnCl₄, and some other analogous compounds.

Study of kinetics of polymerization of acrylonitrile in DMF and

ethylene carbonate at 50 and 60° with utilization as initiators of dinitrile of azoizobutyric and azodicyclohexane-carboxylic acids showed [20] that in this case low-molecular products predominantly are formed.

Page 26.

In the presence of oxygen the polymerization at a temperature of 45-50° not at all occurs. The formation of low-molecular products in these solvents is connected, apparently, with the smaller activity of radicals and with the phenomenon of chain transfer.

Studies by Bamford, Jenkins and Johnston established that during polymerization of acrylonitrile in DMF at 40 and 60° by application as initiator of dinitrile of azodiisobutyric acid and in presence FeCl₃, significant role in reaction of interruption of chain plays process of recombination of polymeric radicals [31]

At analogous conclusion arrived also Ulbricht 36, who investigated of "varnish" polymerization process of acrylonitrile in dimethyl formamide, dimethylacetamide, dimethyl sulfoxide and butyrolactone.

However, up to now yet it was impossible to select such conditions of the "varnish" method of the polymerization of acrylonitrile in the organic solvents, which would provide obtaining products with sufficient molecular weight.

Mechanism of polymerization

There are two forms of polymerization of acrylonitrile: ionic

and radical.

Ionic polymerization is caused by formation of ions under the effect of catalysts. With the ionic polymerization the catalyst is not included in the generatrix of the polymer, with which it is connected, probably, only in the polymerization. The reactions, catalyzed using ions, relate to a number of most rapidly occurring reactions, known in the organic chemistry, and are characterized by the extremely low activation energy. This reaction, having been once begun, energetically is developed up to the explosion; therefore while its conducting it is extremely important to ensure the heat removal. Ionic polymerization almost always is conducted in the solution at low temperatures (from -50 to -130°).

As catalysts are used BF_3 , TiCl_4 , etc., and also metallic sodium in liquid ammonia [37]. Recently [38] was studied the possibility of utilization as the catalysts during the polymerization of acrylonitrile of different hetero-organic compounds. Thus, positive results are obtained during the polymerization xylene with the initiator by the tributylboron, activated by the etherate of boron fluoride. In the presence of such catalysts, which cause the formation of the growing polymer chain with the negative charge at the end, usually is obtained polyacrylonitrile with very light molecular weight [39].

Radical polymerization occurs as a result of molecule activation

of acrylonitrile due to its reaction with free radical, which is generated upon decay of initiator.

Page 27.

This decomposition of initiator can be caused by different reasons: the effect of light/world, heat, ultrasound, radiation or by chemical initiators. The latter include, for example, peroxides and diazo compounds, upon decay of which are tested the dinitrile of azodiisobutyric acid [12], benzoyl peroxide and diazoaminobenzene [11]. of phenylazoalkylmalononitrile [30] and many other analogous compounds. From inorganic peroxides, besides peroxide of hydrogen [1], used in essence over/resulfates, for example $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and perborate of sodium.

Nature of initiator has great effect on polymerization and mainly to speed of its course. So, were shown [11], that the speeds of the copolymerization of butadiene, styrene and acrylonitrile in the presence 1% benzoyl peroxide relate as by 1:50:100 000, and in the presence of the same quantity of diazoaminobenzene they relate as by 1:3:25. In the presence of dodecylmercaptan and pyridine the polymers with molecular weight of less than 1000 are formed. Thus, fractionation isolated the polymers of acrylonitrile with $M = 2800_{\text{max}} = 1700$ [10].

Are established [11], that during application as initiator of persulfate of potassium number of free radicals, which appear as a

result of his decomposition and which initiate polymerization reaction, it is approximately constantly during entire process. This makes it possible to analyze the course of polymerization in time [41]. P. Khomiko'skiy and S. Medvedev [15] they investigated dependence of speed of polymerization of acrylonitrile in aqueous solutions on concentration of monomer, persulfate of potassium and on temperature. The dependence of the speed of polymerization on the concentration of the persulfate of potassium can be explained as follows:

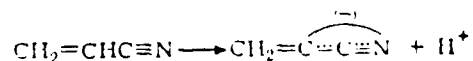
1. Initiation reaction consists of the formation of complex of monomer and persulfate of potassium.

2. Two radicals form this complex with the molecule of monomer.

3. Break of reaction chain occurs: a) due to recombination of growing chain and b) as a result of reaction of active radicals with initiator.

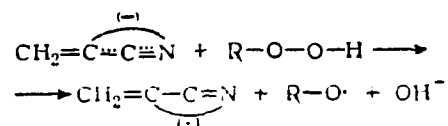
Reaction rate of polymerization is proportional to square root from concentration of persulfate and square of concentration of monomer.

During initiation of polymerization by different peroxides reaction mechanism can be different. T. M. Gritzenko and S. S. Medvedev [42] they allow/assume the possibility of the molecular reaction of peroxide (for example, hydroperoxide of cumol) with acrylonitrile according to the following diagram:



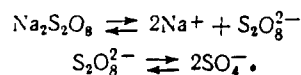
Page 28.

Formed "anion" of acrylonitrile reacts with hydroperoxide:

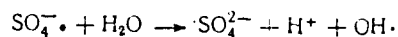


The initiated monomer gives beginning to an increase in the polymer chain.

There is, however, another point of view, expressed by series/number of foreign researchers, in particular Houtz [16]. Free radicals during the polymerization in the presence of persulfates are formed according to the following diagram:



Ionic sulfate-radical is very unstable, and as a result of its reaction with water is formed more stable hydroxyl radical, which initiates in main reaction of polymerization:



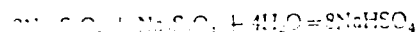
i.e. chain growth is initiated by radicals of hydroxyl.

During polymerization of acrylonitrile under the effect of persulfate induction period lasts sometimes several hours [41]. For the utilization of this method in the industrial scale it is necessary to accelerate the decomposition of persulfate. The decomposition of persulfate in the aqueous solution is accelerated by addition to the

solution of salts of heavy metals. for example silver nitrate [41]. The speed of polymerization can be also considerably increased by introduction to the reaction medium of the substances, oxidized by persulfate. Good reducers are salts of the oxyacids of sulfur, for example thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$, bisulfite NaHSO_3 , and its derivatives: metabisulfite $\text{Na}_2\text{S}_2\text{O}_5$, and hydrosulfite $\text{Na}_2\text{S}_2\text{O}_4$. It is proposed to use for this purpose rongalite $\text{NaHSO}_3 \cdot \text{CH}_3\text{O}$, and also sulfur dioxide.

During utilization for initiation of polymerization of redox systems,

the reaction can be shown by the following diagram.



[15, 16, 42]

It was established that polymerization in the presence of oxidation - reduction systems differs from polymerization initiated by a radical compound, and by the mechanism of formation of the polymer. About this the values of the summary energy of the activation of the polymerization of acrylonitrile testify.

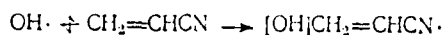
Page 29.

Thus, during the initiation of reaction by one hydroperoxide of cumol the activation energy is equal to 10.1 kcal/mole, and during the addition to the reaction medium of hydroquinone it is reduced to 7.2 kcal/mole [42]. During the initiation by the persulfate of potassium the summary activation energy is equal to 14.2 kcal/mole [15], during the addition to the system of sodium hydrosulfite it is reduced to 11.1 kcal/mole [25]. The value of the energy of the activation of process is changed not only in the dependence on a quantity of added reducer, on and depending on the qualitative composition of redox system. For example, during the utilization of the initiating system, which consists of bivalent iron and peroxide of hydrogen, energy the

activation of activation is 20 kcal/mole [43].

Change in value of energy of activation of polymerization of acrylonitrile is explained, apparently, by rate of formation of free radicals.

To important role of OH-radicals, which facilitate beginning of increase in polymer chain during redox initiation, they indicate Kerber and Patat [44], shown based on example systems hydrogen peroxide - rongalite possibility of forming activated radical complex:



These authors established that initiating capacity of this system does not depend on concentration of reducer - rongalite. At the same time molecular weight of obtained polyacrylonitrile strongly depends on the content of reducer. According to the data of E. S. Roskin [25], with the decrease of the initial concentration of sodium hydrosulfite the second molecular weight of polymer is increased more than 5 times. In practice this procedure - a change in the initial content of reducer in the reaction medium - is frequently used for regulating molecular weight of polymer.

Rate of bimolecular reaction of reaction of persulfate with reducers - layers of oxygen compounds of sulfur - considerably increases/grows in presence of metal ions in by variable/alternating valence, for example Cu^{2+} and Fe^{3+} . Even in a quantity of ten

thousandth fields of percentage these ions substantially influence the flow of entire polymerization reaction. Therefore in the production of polyacrylonitrile it is necessary to track the fact so that the content of metal indicated ions would be constant, since with the nonobservance of this condition the speed of polymerization and molecular weight of the obtained polymer will strongly oscillate. For this very reason special attention should be given to the thorough purification of water. In the presence of a significant quantity of salts of these metals in the water the oxidizer and reducer can rapidly react between themselves, as a result of which the polymerization of acrylonitrile will be decelerated or altogether will be interrupted.

Page 30.

For decreasing oscillation/vibration ion concentration of heavy metals [24] proposed to introduce into mixture to 0.005% $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$.

In this case common oscillations in the impurity content - the tracks of metal ions with the variable/alternating valence - are smoothed.

Degree of reaction of persulfate with reducer depends on pH medium. Thus, Ye. S. Roskin [25] showed that with an increase in the concentration of sulfuric acid from 0.2 to 0.5 g/l in the polymerization of acrylonitrile with the application of a system the persulfate - sodium hydrosulfite degree of polymerization increases/grows 5 times. At the analogous conclusion they arrived

Yuguti and Vatanabe [40], investigated effect of pH on the speed and degree of polymerization of acrylonitrile in the presence of the initiating system persulfate - triethanolamine. It was shown that decrease pH conditions deceleration of polymerization and increase in the degree of polymerization of the generatrix of polymer. For regulating pH the medium it is expedient to use buffer solutions. The quality of the obtained polymer (value of molecular weight, the degree of branching, etc.) it is determined to a considerable degree also by the presence of the surface-active compounds, which are the carriers of chain, for example mercaptans [45], different alcohols [46], in particular methyl and isopropyl alcohol, and also different aldehydes and ethers/esters [22].

Initial temperature of polymerization has great effect on speed of polymerization and quality of obtained polymer. With an increase in the initial temperature of polymerization 2 times (from 20 to 40°) the speed of polymerization increases/grows into 8-9 times.

Solubility of generatrix of polyacrylonitrile to a considerable degree depends on temperature of polymerization [47]. The polymer, which is generated in the polymerization of acrylonitrile in the aqueous solution at 20-50° in the presence of redox initiators, is dissolved in the DMF at room temperature; the polymer, obtained at a temperature of polymerization of 70-75°, is dissolved in the DMF at 60-70°.

Thus, polyacrylonitrile it is simplest to obtain by polymerization in aqueous medium in presence of water-soluble initiators. During the dilution of acrylonitrile by water polymerization to more easily regulate, furthermore, polymer in this case settles in the form of the fine/small easily filtered granules.

It is necessary to consider exothermicity of process, since heat, which separates during polymerization, is comparatively great and is 17.3 kcal/mole [19], and depending on degree of heating reaction mixture is changed molecular weight of polymer. It is lowered with an increase in the temperature of polymerization.

Page 31.

Molecular weight of polyacrylonitrile is changed also in dependence on activity of initiating system, pH of medium and on content of metal ions with variable/alternating valence: it increases/grows with decrease of activity of initiators and is reduced with increase pH of system and increase in content of metal ions with variable/alternating valence.

Thus, regulating removal of heat, which separates during reaction, is changed rate of process and they attain formation of polymers with assigned molecular weight. For the wet spinning of polyacrylonitrile fiber usually use polymers with molecular weight of 50 000 - 60 000; for the dry spinning are used the polymers from by somewhat smaller molecular weight (35 000-45 000). In order to obtain

standard product, it is necessary to strictly observe all conditions for technological process.

From components, undertaken for reaction, should be thoroughly purified impurities. For the polymerization it is necessary to use freshly distilled acrylonitrile, which contains not more than 1% water. During the prolonged storage of acrylonitrile its activity is decreased. Special attention must be paid to thorough removal of divinylacetylene from acrylonitrile; its content in acrylonitrile must be minimum. An absolute quantity of divinylacetylene, which is present in acrylonitrile, must not be changed, since it influences the duration of the induction period of polymerization.

Oxygen is inhibitor of polymerization of acrylonitrile; in its presence large induction period [48] is observed. If in the reaction medium long time was located dissolved oxygen, then in the system the sufficiently high concentrations of free radicals is not created, and polymer is not formed. Kerber [49] investigated the influence of oxygen on the polymerization of acrylonitrile in the presence of dinitrile of the azoisobutyric acid, undertaken as the initiator. He established that the elongation of induction period in the presence of oxygen is caused by the formation of high-molecular peroxides, soluble in the monomer and in many solvents. Molecular weight of such intermediate products can exceed 6000. In connection with this it is desirable to give the polymerization of acrylonitrile in the atmosphere of nitrogen.

Obtaining dry product.

After completion of polymerization they drive off polyacrylonitrile from aqueous phase on nutsch filters, on vacuum drum filters or on centrifuges. Then they thoroughly wash clean it from the remainders/residues of unreacting acrylonitrile and different salts.

Page 32.

With the poor washing of polymer in the spinning solution the fractions/particles of gel [24] are formed. Wash water must not contain more than 110 mg/l of the ions of chlorine (in the recount on NaCl) and more than 130 mg/l of the ions of sulfate (in the recount on Na_2SO_4).

During total spending of monomer danger of obtaining very polydispersed product appears; furthermore, is possible chain transfer to inactive macromolecules of polymer, which leads to formation of branched molecules. Therefore they conduct process until 70-80% of monomer react. Because of this the need for the regeneration of the unreacting monomer from the filtrate (after the separation of precipitate) and from the wash waters appears. For the same reason for an improvement in the working conditions it is necessary not only to thoroughly seal the reactor, in which the polymerization is conducted, but (in order to prevent the possibility of the entry of

vapors of acrylonitrile into working room) to supply the suspension of polymer from the liquid phase and the suction of the separating vapors of acrylonitrile.

Acrylonitrile they regenerate via its distillation/removal with water vapor or in vacuum. They return the regenerated monomer to the production.

For obtaining standard spinning solutions from its polyacrylonitrile after washing thoroughly they dry. The moisture content in the polymer there must not exceed 0.5%. The process of drying they conduct at 70-80° in the chamber, strip/tape or shaft driers during 36-50 hour. The temperature of drying has an effect on the solubility of polyacrylonitrile. Thus, after drying at 70-80° it is dissolved [47] at 20°. But if we the preparation of polyacrylonitrile, dissolved in the dimethyl formamide at room temperature, upset from the solution, and then to heat to 110-120°, then its solubility is considerably worsened, and the minimum temperature, in which it is completely dissolved is raised to 30°. At the same time the viscosity of the solution will be considerably increased 2-3 times. This is explained, apparently, by an increase in intensity of interaction of the nitrile groups of one chain and hydrogen atoms of

Thus, for obtaining good spinning solutions polymer must be dried at lowest possible temperature (desirably in vacuum).

They crush dried out polyacrylonitrile on spherical or disk mill,

after which it are packed (see Fig. 5). For facilitating the process of dissolution it is necessary that the value of the particles of the ground polymer would be minimum (not more than 0.5-1.0 mm). It is necessary to at the same time consider that powdery polyacrylonitrile forms in by air very dangerously explosive mixtures. Therefore with the ground product of polymer the corresponding precautionary measures take.

Page 33.

Obtaining copolymers.

As is known, the articles, obtained from polyacrylonitrile under the normal conditions, are characterized by brittleness and badly/poorly are stained. By copolymerizing acrylonitrile with other monomers (vinyl acetate, vinylpyridine, etc.) of property it is possible to considerably improve.

Capacity of some monomeric compounds to be united between themselves with formation of new complex high-molecular substances was established/installed in 1887 by Russian chemist V. Solonin [50].

Each monomer, which forms part of copolymer, it communicates to it its specific properties. Using different combinations of monomers, it is possible to create copolymers with the desired combination of properties. B. N. Rutovskiy [51] investigated the dependence of the properties of copolymers on nature of the monomers entering in them. He showed that the properties of copolymers were different from the simple sum of the properties of the mechanical mixture of the polymers, obtained from each monomer individually. The change in the properties, caused by the introduction of each monomer to macromolecule, on is proportional to its quantity [52].

At present it is known more than 400 forms of copolymers of acrylonitrile with different monomers. From them about 300 are proposed for obtaining the fibers. The copolymer, which contains 40% of vinyl chloride and 60% of acrylonitrile, is capable to be dissolved in acetone. Articles made of the polymers, obtained during the copolymerization of acrylonitrile with 4-5% of vinylpyridine, are stained with acid dyes. By copolymerization can be obtained products from the hydrophilic, strongly swelling in the water substances, to the completely undissolved polymers.

It is interesting to note that solubility of copolymers of acrylonitrile, which contain small quantity of second component (5-10% of weight of copolymer), after their heating is not reduced, obviously, as a result of smaller probability of additional formation of hydrogen bonds.

Frequently for improvement in combination of properties of polymer is conducted copolymerization of acrylonitrile with two and more by monomers.

In quantity of acrylonitrile in copolymer all copolymers of acrylonitrile can be conditionally divided into two large groups:

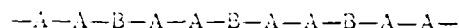
- 1) copolymers, which contain are more than 85% acrylonitrile;
- 2) copolymers, which contain are less than 85% acrylonitrile.

Linear and branched (grafted) copolymers are obtained by copolymerization of acrylonitrile with other monomeric compounds.

Page 34.

The macromolecular chains of linear copolymers can be three types:

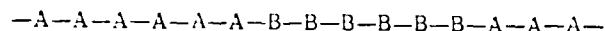
- a) the regular alternating of the heterogeneous monomer units:



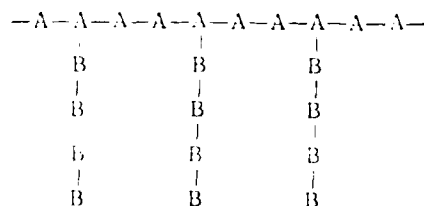
- b) accidental, random distribution of monomers on chain:



- c) polymer chain is constructed from large "blocks", each of which contains only one form of monomer



Under specific conditions of copolymerization are formed those branched - graft polymers (frequently called graft copolymers) whose main chain of polymer consists of one form of monomer, and lateral branches - of another. Schematically a copolymer of such type can be depicted as follows:



In the vicinity of these monomer units are furnished in a linear polymeric form or is less or trace. In a certain sense, the physicochemical nature of polymer becomes complicated. It is characterized by not only the polydispersion, but also the

the individual fractions of polymer have the dissimilar chemical composition. However, while conducting of copolymerization under certain conditions it is possible to obtain copolymer with the regular arrangement of monomer units along chain [53].

As is known, properties of high-molecular substances are determined to a considerable degree by structure regularity of macromolecules, since on this reaction of intermolecular forces depends. During the copolymerization it is possible over wide limits to change structure regularity thereby to influence the properties of the obtained product. As a result of introduction to the molecular chain of different monomer units the regularity of the structure of chain is disturbed. If in this case simultaneously is decreased intermolecular interaction (as, for example, during the introduction of 8-10% vinyl acetate), then the solubility of polymer and its elasticity are raised, but in this case softening temperature is reduced. During the copolymerization of acrylonitrile with the substances, which amplify intermolecular interaction (for example, with acrylamide), the brittleness of articles considerably increases/grows. The elasticity of polymer depends also on the density of the packing of macromolecules. As [54] were shown, the maximum density of the packing of the molecular chains frequently corresponds to the greatest hardness and the brittleness of the obtained copolymers and vice versa.

While conducting of process of copolymerization should be focused attention on two facts:

1. Each monomer, which enters in the reaction of copolymerization, reacts with different speed; because of this the composition of copolymer it can not correspond to the composition of initial monomeric mixture ¹.

FOOTNOTE ¹. In more detail about the effect of different factors on the process of copolymerization see in appendix I. ENDFOOTNOTE

2. In the reaction of copolymerization can enter such monomers, which individually under the same conditions usually are not polymerizable. Thus, ethers/esters of maleic acid do not enter into the polymerization reaction; at the same time they comparatively easily form copolymers with acrylonitrile.

All copolymers of acrylonitrile, intended for treatment/processing into fiber, are obtained by common methods of synthesis - emulsion polymerization and by solution polymerization.

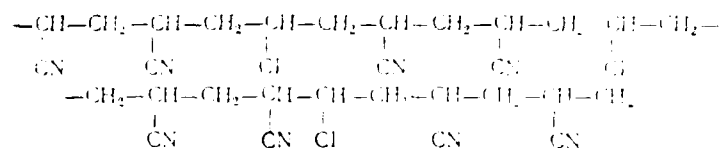
As example method of synthesis of copolymer of acrylonitrile with methylmethacrylate, developed in All-Union scientific research institute of artificial fibers by G. I. Kudryavtsev and M. A. Zharkovoy can be given. Polymerization conducted in the emulsion with the relationship/ratio the monomer: water, equal to 1:3. The emulsification of monomer was achieved by addition 3% of mersolate of

sodium. As the initiator they used 0.3% (from the weight of monomers) of the persulfate of potassium. In order to avoid the formation of the side chains, into the reaction mixture they introduced by 0.25% of thymol. Reaction conducted at 50° during 2.5 hour. The initial mixture of monomers consisted of 90% of acrylonitrile and 10% of methylmethacrylate; in the copolymer it was contained by 82.6% of acrylonitrile and 17.4% of methylmethacrylate. The subsequent treatment/processing of copolymer (washing, drying, grinding) was performed just as the polymer, obtained only from acrylonitrile.

There are two methods of copolymerization. Using the first method the mixture of monomers in the required relationship/ratio is taken immediately.

Using the second method of the second of components they introduce into the process gradually. In this case the product is more uniform.

Usually in process of copolymerization monomers are united between themselves according to principle "head to tail", but can be formed copolymer of type "head to head". Thus, the copolymer of acrylonitrile with the vinyl chloride can have two structures:



Therefore during the estimation of the quality of copolymer together with its polydispersion is considered both the chemical heterogeneity of the macromolecules of different length and macromolecules with identical molecular weight, but with different chemical structure.

Third type of linear copolymers, called block copolymers, is very interesting.

Block copolymers, i.e., copolymers, which consist of unit of monomer A and unit of monomer B, are obtained as a result of conducting process of copolymerization under special conditions. It is known that "the polymer gives birth to polymer". If into the reaction medium, in which there is a dispersed polymer, to introduce any new monomer, then polymer, acting as "active center", contributes to the polymerization of the introduced monomer. The example of obtaining the block copolymer of acrylonitrile and methacrylonitrile [55, 56] is given below.

Methacrylonitrile in quantity of 100 pbw mix from 300 pbw, water, 1 pbw of lauryl sulfate of sodium, undertaken as emulsifier, and 1 pbw of persulfate of potassium. They thoroughly mix mixture and heat at 100° during 6-8 min., and then they cool to 25°. As a result of reaction entire methacrylonitrile is polymerized. Then into the reaction mixture 50 pbw are added. Acrylonitrile is continued process at the same temperature. After all acrylonitrile reacts, they

separate polymer from the reaction medium, they wash and dry. The investigation of the obtained product is shown that the polymer chain consists of the sections of the acrylonitrile links, connected with the sections of methacrylonitrile links. As is known, methacrylonitrile is completely soluble in acetone, but polyacrylonitrile in acetone even will not swell; the obtained block copolymer forms stable dispersion in acetone.

Properties of block copolymers sharply differ from properties of common copolymers of identical composition. Fig. 6 gives softening temperatures of common copolymers and block copolymers of acrylonitrile and acrylamide of different chemical composition [57]. In the physical properties the block copolymers approach mixtures of polymers, but qualitatively they are different from the mixtures.

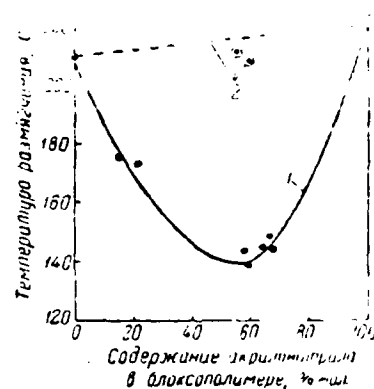


Fig. 6. Effect of chemical composition of copolymer of acrylonitrile and acrylamide on softening temperature: 1 - common copolymer; 2 - block copolymer.

Key: (1). Softening temperature. (2). Content of acrylonitrile in block copolymer, % mole.

Page 37.

A qualitative difference in the block copolymers from the mixture of polymers is in the fact that they are new chemical compound; whereas the mixture of polymers can be divided by thorough fractionation into the chemically individual components.

Of significant interest are "grafted" copolymers, or graft copolymers. With graft copolymerization of the second of components "is inoculated" to the basic polymer chain, forming the branch of another chemical composition. It is possible to obtain such copolymers, which it is impossible to obtain normally, for example the copolymers of polyvinyl alcohol and acrylonitrile, or polyethylene and acrylonitrile by this method. Heating polyacrylonitrile latex with

vinyl acetate in the presence of the persulfate of potassium at 60° during 16 hours, is obtained the compound, in which to the polyacrylonitrile chain "are grafted" the branches of vinyl acetate [58].

Hunyar and Reichert [47] synthesized "grafted" on polyacrylonitrile copolymers with vinyl acetate and acrylic acid and compared properties of fibers, molded from these copolymers, with properties of fibers, obtained from common copolymers of the same composition, but synthesized by generally accepted methods. In the copolymer, which is formed as a result of "inoculation" on the polyvinyl alcohol of acrylonitrile, in the side chains it is contained to 95% of acrylonitrile, which entered the reaction.

Presence of long side chains in macromolecule of graft polymer did not condition noticeable reduction in physicomechanical properties of obtained fibers. Shapiro [59] obtained the copolymers of acrylonitrile, grafted on polyethylene, by radiochemical method and studied the swelling of films from this product in the DMF. He established that at room temperature of the noticeable swelling of product he is not observed; at 100° the graft polymer will swell very intensively. The graft polymers are dissolved somewhat worse than the common copolymers of the same composition, and their solutions rapidly are gelatinized. According to the physicomechanical properties the fibers, molded from the graft polymers, are virtually identical to fibers from the common copolymers, but they are somewhat more inclined

to the contraction in the hot water.

Under certain conditions it is possible to obtain completely soluble copolymers.

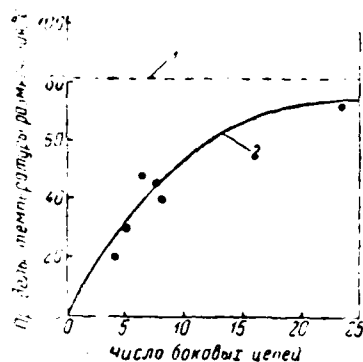


Fig. 7. Effect of quantity of side chains on softening temperature of graft polymer of acrylonitrile and acrylamide: 1 - common copolymer; 2 - graft polymer.

Key: (1). Limits of softening temperature. (2). Number of lateral chains.

Page 38.

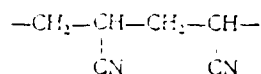
With an increase in the number of the side chains the physical properties of the graft polymers of acrylonitrile and acrylamide approach properties of the common copolymer of the same composition [57] (Fig. 7).

Question about worthwhileness of synthesis of graft copolymers of acrylonitrile for preparing fiber up to now is not resolved.

Properties of polyacrylonitrile.

Polyacrylonitrile is white powder-like substance with bulk weight of 200-250 g/l and ud with weight of 1.14-1.15 g/cm³. About the

structure of the molecules of this polymer the data, obtained by chemical methods, at present no. It is assumed (by analogy with other carbon-chain polymers) that as a result of the polymerization of acrylonitrile is formed the substance of the following structure:



According to available very scarce roentgenographic data also it is not possible to make specific conclusions about structure of this polymer. The X-ray photographs of the fibers, subjected to different degree of stretch, are characterized by the presence of the diffusion rings, which attest to the fact that the crystalline regions in this polymer are very small or very inadequate, i.e., common polyacrylonitrile, similar to polyvinyl chloride, it is incapable, possibly, to the crystallization. On the distance between the layer lines in the X-ray photographs molecular period (texture) was determined. According to the data of Becker [60], it is equal to 5.20 Å; according to the data of Ham [29] - 5.0 Å. Since available for polyacrylonitrile roentgenographic data are very indistinct, then on their basis/base it is not possible to make any conclusions about the stereochemical regularity of the structure of the molecules of this polymer. On the obtained X-ray photographs of polyacrylonitrile it is possible to assume that the presence of the groups of $-CN$ in the position of 1.3 carbon chains conditions the twisting of the chains of macromolecules into the spiral. The fact that polyacrylonitrile even with the high degree of the orientation of macromolecules does not give sharp crystalline picture, apparently, is explained by the

following:

1. In the large measure is probable the geometric irregularity, which can be caused by the fact that the lateral nitrile groups occupy, apparently, in some sections of chain arbitrary left and right position. Such disordered sections cannot be crystallized [61].

2. In polymerization of acrylonitrile monomer units are united according to type "head to head" or according to type "head to tail".

Page 39.

Consequently, polyacrylonitrile can not have regular chemical structure.

Spectrographic of investigations [16] give certain presentation/concept about chemical structure of polyacrylonitrile; their results confirm that monomers are united predominantly according to principle "head to tail".

Polyacrylonitrile possesses high heat resistance.

Are cited below data about temperature of decomposition in air of different fiber-forming polymers:

Temperature of decomposition °C.

Perchlorovinyl ... 145-150.

Polyvinyl chloride ... 150-155.

Polyvinyl alcohol ... 150-170.

Cellulose acetate ... 210-220.

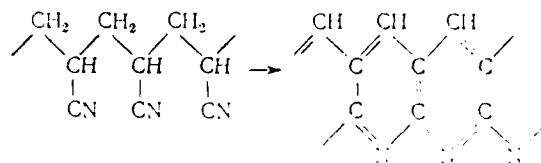
Cellulose ... 210-230.

Polyacrylonitrile ... 220-230.

Similar to majority of other carbon-chain polymers, polyacrylonitrile under normal conditions it is not melted; at 220-230° it is softened and simultaneously is decomposed/expanded. [29] theoretically calculated the melting point of polyacrylonitrile, on the basis of the fact that the temperature of the transition of polyacrylonitrile from glassy to highly elastic state was equal to 90°. According to its calculations, the hypothetical melting point of polyacrylonitrile composes 269°. Through others data [60], it is found in the range from 290 to 300°.

They investigated change in properties of polyacrylonitrile during heating (up to pyrolysis) repeatedly. By the purpose of these works it was find such conditions, with which the polymer would be in the molten state and in this case it did not occur its destruction; the resolution of this question would make it possible to considerably simplify the problem of obtaining fibers from polyacrylonitrile.

Kobajaci [62] conducted spectrographic investigation of dissolved polyacrylonitrile, subjected to prolonged heating at 100°. It noted the appearances of new absorption bands, connected with a change in the structure of the polymer chain. Ham [29] considers that during the heating to the temperature higher than 100° the intra-chain cyclization of polyacrylonitrile according to the diagram



can occur.

During heating of polyacrylonitrile up to 120° of its volatile products [63] are separated/liberated.

Page 40.

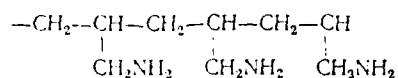
During further prolonged heating in the presence of atmospheric oxygen the polymer darkens. Initially it becomes yellow, then red and, finally, brown. Simultaneously polymer is made by that not dissolved. As has already been indicated, the solubility of polymer considerably is decreased even after drying at 80°; the quality of spinning solution of this polymer it is worse than from the polymer, dried out at 60-70°.

In common stable polyacrylonitrile polymers, used for preparing fibers, color must not be changed during their heating to 170-180°. In the work of Grassi and MacNeill [63], thermal decomposition of polyacrylonitrile and change in this case in its color is accelerated

due to the presence in the polymer of admixtures/impurities. If we as the initiator of polymerization apply dinitrile of azoisobutyric acid and all components of reaction thoroughly to purify, product is thermostable. The copolymers of acrylonitrile, which contain even a very small quantity of second component, are considerably more subjected to thermal destruction, than pure/clean polyacrylonitrile.

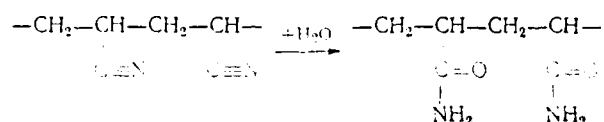
During intensive heating of polyacrylonitrile to 250-300° pyrolysis of polymer occurs. The investigations of the pyrolysis of polyacrylonitrile [64] without the access of oxygen in the range of temperatures from 220 to 320° showed that in this case hydrogen cyanide and ammonia are separated/liberated mainly. The obtained simultaneously liquid distillate contains different nitriles, amines and unsaturated compounds.

Polyacrylonitrile is capable to react with different compounds with appropriate transformation of nitrile groups. Were studied [65] processes of hydrogenation, saponification and ether/esterization of polyacrylonitrile. The investigation of the products of chemical transformations during the polymer-analogous transformations occur the processes of the reaction of functional groups, which lead to the cyclization in the chain of polymer. Thus, during the hydrogenation of polyacrylonitrile reaction product is not compound of the type



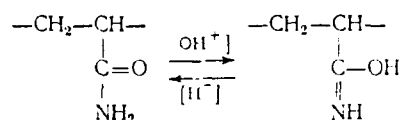
and the polymer, which consists predominantly of the remainders/residues of piperidine.

During alkaline or acid saponification of polyacrylonitrile into heterogeneous medium nitrile groups are converted into amide:



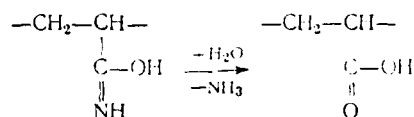
Page 41.

This reaction occurs the more intensive, the higher temperature. Generating amide comparatively easily will be hydrolyzed to the acid. The possibility of the enolization of amide according to the equation



contributes to this.

Amide generating in enol form is very unstable and easily (with splitting NH_3) it is converted into acid [66]:



Chemical resistance of polyacrylonitrile in comparison with polyvinyl chloride is considerably below. Under the effect of the acids and the alkalis polyacrylonitrile is saponified partially or completely with the formation of polyacrylamide or salts of polyacrylic acid. In the concentrated sulfuric acid polyacrylonitrile

is dissolved: under the effect/action of ammonia and amines it darkens as a result of the formation of amidine compounds [67]. But polyacrylonitrile is resistant over a wide range of temperatures to the effect/action of different alcohols, organic acids (with exception of formic), hydrocarbons, oils, ketones, ethers/esters and other substances.

Houtz [16] observed, that sodium hydroxide exerts strong destructive action on polyacrylonitrile, dissolved in DMF. For example, according to his data during the addition to 5 g of the polymer, dissolved in the DMF, 0.001 moles of the sodium hydroxide molecular weight of polyacrylonitrile are reduced less than in 1 s. from 110000 to 19000. To the effect/action of alkalis polyacrylonitrile is less resistant than to the effect/action of acids.

In Table 1 data about chemical resistance of some fiber-forming polymers [68] are cited.

In large measure properties of polyacrylonitrile and its capability for treatment/processing are determined by molecular composition of product. However, there is at present very few works, dedicated to this important question. As is known, molecular weight of any polymer is average value, and its value depends on the method of determination. During the viscometric determinations the weight averages of molecular weight are obtained, while during the osmometric

determinations - numerical average. In the polymer the specific distribution of macromolecules along the lengths of chain, which depends on the special features of conditions of polymerization, is always observed.

Page 42.

Therefore for the characteristic of polyacrylonitrile together with medium molecular weight of polymers it is necessary to know the distribution of polymeric molecules by molecular weights or along the lengths of chain. The most detailed investigations in this region were carried out by Houtz [16] and Hunyar [69].

Houtz considers that numerical average molecular weight of polyacrylonitrile, used for preparing fiber, must be located in range from 40000 to 80000. After using the procedure, proposed by Lanzl, Houtz [16] determined the polydispersion of polyacrylonitrile by settling by n-hexane of fractions of polymer and with different molecular weight from 2% solutions in DMF at 60°. It is known that the ratio of weight-average molecular weight to the numerical average can serve as the characteristic of the degree of distribution by molecular weights. This relationship/ratio usually vary within the range of 1 to 2.

Table 1. Chemical resistance of some fiber-forming polymers. (The conventional designations: ++ it is highly stable; + it is stable - it is unstable).

Реагент	Кон- цент- рация %	Темпе- рату- ра °C	Поли- акри- лонит- рил	Пер- хлор- винил	Капр
Азотная кислота (7)	Дымя- щая	20	—	++	—
	40	40	—	++	—
	35	50	—	++	—
	10	90	+	++	—
Серная кислота (10)	96	20	—	+	—
	90	20	+	++	—
Соляная кислота	38	20	—	++	—
	38	50	—	++	—
	38	100	—	++	—
Чистая вода	100	75	—	+	—
Фосфорная кислота (12)	85	100	—	+	—
Едкий натр (13)	50	50	—	++	+
	25	100	—	++	+
Аммиак (15)	28	20	+	++	++
	5	25	++	++	++
Хлористый цинк (16)	50	75	—	++	++
Роданистый кальций (14)	50	100	—	++	++
Гипохлорит натрия (11)	5,25	50	+	++	+
	20	65	—	++	—
Перманганат калия (18)	2	100	+	++	++
	4	100	—	++	++
Уксусная кислота (19)	100	65	+	++	—
	50	50	++	++	—
Муравьиная кислота (20)	100	50	—	+	—
	25	50	+	++	—
Фенол (21)	90	20	++	++	—
Анилин (22)	100	20	—	—	—
Пиридин (23)	100	20	—	—	—

Key: (1). Reagent. (2). Concentration %. (3). Temperature of °C. (4). Polyacrylonitrile. (5). Perchlorovinyl. (6). By Kapr. (7). Nitric acid. (8). Fuming. (9). Sulfuric acid. (10). Hydrochloric acid. (11). Aqua regia. (12). Phosphoric acid. (13). Sodium hydroxide. (14). Ammonia. (15). Zinc chloride. (16). Thiocyanate calcium. (17). Sodium hypochlorite. (18). Potassium permanganate (19). Acetic acid. (20). Formic acid. (21). Phenol. (22). Aniline. (23). Pyridine.

If relation is equal to one, then there is completely a uniform fraction; but if it approaches two, then polymer differs in terms of the wide region of distributing the molecules along the length. Because of this the ratio of weight-average molecular weight to the numerical average it is the important value, which makes it possible to compare distribution with respect to molecular weights of different samples of one and the same polymer. For polyacrylonitrile this relationship/ratio [16] is equal approximately to 2, i.e. polyacrylonitrile is very polydispersed product.

Was investigated [69] effect of polydispersion and average molecular weight on spinning conditions and property of obtained fiber. For an increase in the polydispersion of polyacrylonitrile the samples of polymer with different molecular weight are mixed between themselves. With molecular weight of polyacrylonitrile of lower than 10000 to form fiber proved to be generally impossible. The more polydispersed polyacrylonitrile and the more in it it is contained low-molecular fractions with molecular weight of less than 10000, the worse the property of the obtained fiber, the less the maximum degree of stretch. [29] were shown, that for the spinning of fiber the polymer with molecular weight of about 35000 is most suitable. The specific viscosity 0.1% solution of this polymer in the dimethyl formamide is equal to 0.19.

For determination of molecular weight of polyacrylonitrile in solution according to viscometric data are proposed several equations:

Concentration of initiator, M	η_{sp}/C	Concentration of initiator, M	η_{sp}/C
$[I] = 1.5 \cdot 10^{-4} M$	70	$[I] = 3.0 \cdot 10^{-4} M$	71
$[I] = 2.5 \cdot 10^{-4} M$	72	$[I] = 3.0 \cdot 10^{-4} M$	72
$[I] = 2.43 \cdot 10^{-4} M$	73	$[I] = 3.45 \cdot 10^{-4} M$	65

Key: (1). Reference on the literature.

For determination of molecular weight distribution of polyacrylonitrile were proposed also thermal-diffusion [74], sedimentation [72] and other methods.

Polydispersion of polyacrylonitrile, obtained by different methods, was widely investigated N. M. Beder and by T. S. Molovoy. These researchers developed the new method of fractionation by turpentine 1-2% solution of polymer in the dimethyl formamide. Were isolated 9-11 fractions, whose molecular weight differed between themselves 8-9 times. Furthermore, it is shown that with the common methods of the polymerization of acrylonitrile the polydispersion proves to be very significant and depends on chemical nature of the selected initiator.

Up to now yet there is not sufficiently substantiated data about optimal molecular composition of polyacrylonitrile, its optimal average molecular weight and effects of these factors on operating characteristics of fiber.

Pages 44-45.

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Page 46.

Chapter 4.

PREPARATION OF THE SPINNING SOLUTION.

At present is not yet found method of spinning from fusion/melt of polyacrylonitrile, so AK this polymer in conditions of production of polyamide and polyester fibers (caprone, Lavsan, etc.), without having been yet fused, it is decomposed/expanded. Therefore they form polyacrylonitrile fiber from the solution, selecting solvents.

It is already long ago known that polyacrylonitrile is soluble in concentrated sulfuric acid and that obtained solutions are sufficiently stable. However, during molding of this solution in the water/aqueous precipitation bath the nitrile groups of polymer rapidly will be hydrolized and fiber is obtained poor quality [1]. Later it was established that polyacrylonitrile is dissolved in the concentrated solutions of some salts, for example in the solutions of halides, perchlorates and thiocyanates of some alkaline and alkaline earth metals [2], and also in the solutions of lithium bromide and zinc chloride [3]. However, to obtain fibers suitable for the textile treatment/processing from the salt solutions for long did not succeed. Only later was developed the method of the spinning of fibers of the solutions of polyacrylonitrile in the solution of thiocyanate sodium

or calcium [3] on the precipitation method in the water at temperatures lower than 10°. At present this method finds increasing use.

Almost simultaneously with discovery/opening of solvency of solutions of inorganic salts with respect to polyacrylonitrile it was established that this polymer can be dissolved in solutions of some quaternary ammonium salts (for example, benzyl-pyridinechloride). In 1942 in Germany [1], and after several years in USA [4] were established that polyacrylonitrile was soluble in the dimethyl formamide (DMF) and in some other polar organic matter. Is at present investigated dissolving with respect to polyacrylonitrile effect/action of many inorganic and organic solvents; they are done alsoⁱⁿ the attempt to theoretically base the process of the dissolution of this highly polymeric substance.

In this book there is no possibility to in detail present theory of dissolution of polyacrylonitrile. Therefore we will be restricted only to short communications/reports about the available experimental and theoretical material.

Page 47.

Physical chemistry of the process of the dissolution of polyacrylonitrile.

It is first of all necessary to establish/install reason for poor

solubility of polyacrylonitrile in common solvents and to determine principle of selection of its dissolving substances.

It is known that during dissolution of high-molecular substances generally and polyacrylonitrile in particular it is necessary to consider following factors:

- 1) flexibility of macromolecules;
- 2) intensity of interaction of macromolecules with each other;
- 3) intensity of bond of molecules of solvent between themselves;
- 4) intensity of reaction of molecules of polymer and solvent.

First factor, i.e., change in entropy of system upon transfer of polymer into solution, depends on change in mobility of molecules of solvent and solvend in obtaining of solution and is connected with mutual arrangement of separate links of macromolecular chains or whole polymeric molecules. Remaining three factors depend on the energy reaction of molecules and are connected with the heat content of system polymer - solvent.

Dissolution flows/occurs spontaneously only in such cases, when process is accompanied by decrease of free energy of system. A change in the free energy is determined by the second law of thermodynamics, according to which

$$\Delta F = \Delta H - T\Delta S$$

where ΔF - change in the free energy of system;

ΔH - change in the inner energy of system during the dissolution;

T - absolute temperature of process;

ΔS - change in the entropy of system.

Fraction/portion of change in free energy, which falls to each component of system (polymer and solvent), is called chemical potential. A. A. Tager [5] she proposed to evaluate the solvency of solvent according to the thermodynamic affinity between the solvent and the solute. A change in the chemical potential of polymer and solvent in the beginning and at the end of the process is the measure of this affinity.

Dissolution of nonpolar compounds (for example, natural rubber in gasoline) is not accompanied by thermal effects, i.e., $\Delta H=0$, whereas dissolution of polyacrylonitrile - exothermic process. For example, according to the data of the authors, the thermal effect of the dissolution of polyacrylonitrile in the dimethyl formamide is sufficiently significant and equal to 640 cal/mole.

Page 48.

One should, however, consider that thermal effect of dissolution is not always measure of affinity between polymer and solvent [6]. Values ΔH about ΔS in the equation of the second law of thermodynamics can be positive or negative, but if dissolution occurs, then the relationship/ratio between them must be such that the value ΔF would be negative value [7].

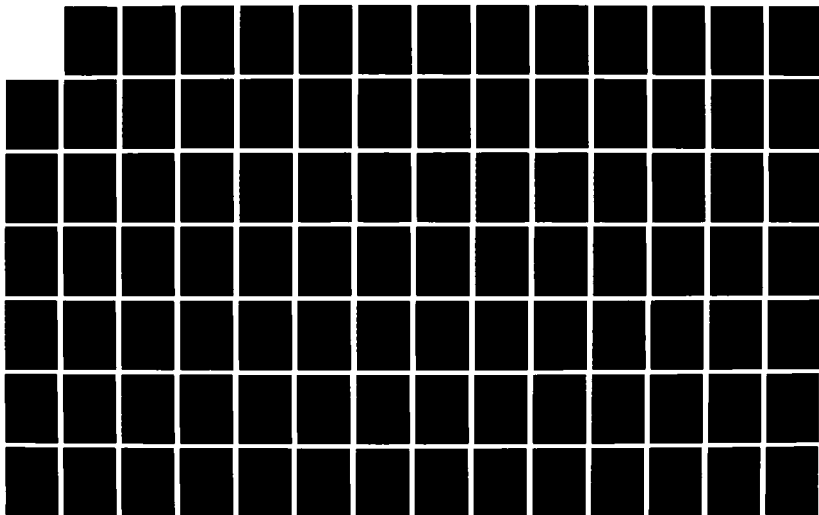
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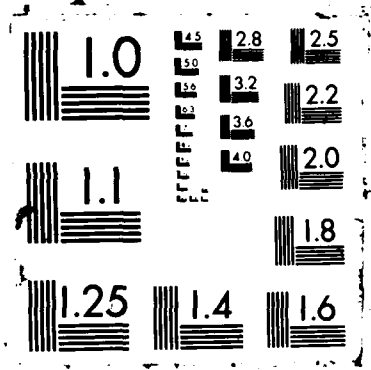
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Value ΔH is connected with interaction energy of separate components of solution with each other. If the intensity of intermolecular interaction in the polymer or the solvent is considerably higher than their affinities for each other, then dissolution will not occur. During the dissolution the bonds between the uniform molecules must be torn and the new bonds between the polymer and the solvent are formed. Thus, ΔH it is the algebraic sum of the separated and exchanged heat, i.e.,

$$\Delta H = \Delta H_{n-n} + \Delta H_{p-p} - \Delta H_{n-p}$$

where ΔH_{n-n} and ΔH_{p-p} - change in the heat content with the break of molecular bonds respectively in the polymer and in the solvent;

ΔH_{n-p} - change in the heat content during the reaction of polymer with the solvent.

For evaluating intensity of reaction of molecules of each component in solution are proposed to calculate "energy density of cohesion" e , i.e., energy, necessary, in order to divide all molecules, which are found in 1 cm³ of pure/clean substance, and to overcome forces of intermolecular interaction. This value can be calculated by the formula

$$e = \frac{L_v - \mu RT}{V}$$

where L_v - heat of vaporization with temperature T , cal/mole;

μ - relation, equal to PV/RT (according to data [8]);

R - universal gas constant;

T - absolute temperature, °K;

V - molar volume of component.

For majority of substances, which boil it is higher than 50°, μ can be accepted by [9] equal to 1.

Sometimes instead of "energy of cohesion" use value $\delta = \sqrt{e}$, characterized as "parameter of solubility" [10]. Hildebrand [11] showed that for the nonpolar and weakly polar polymers and the solvents

$$\Delta H = V_m(\delta_p - \delta_n)^2 V_p V_n$$

where V_m - total volume of solution;

V_p and V_n - parts of the total volume, occupied respectively with solvent and polymer;

δ_p and δ_n - parameters of solubility.

Page 49.

Mathematical analysis of given equation shows that δ_p and δ_n cannot considerably differ from each other, otherwise value $(\delta_p - \delta_n)^2$ [2] will be large. This means that the absolute value ΔH will be more than $T\Delta S$ and, consequently, ΔF will take positive value. In other words, dissolutions will not occur, if δ_p will differ from δ_n by value greater than $1.5 (\text{cal/cm}^3)^{1/2}$.

Estimate of the magnitude δ can be highly useful for substantiated selection of adequate/approaching solvent. Value δ at a temperature T can be obtained from the data about the molar heat of vaporization L_v and about the molecular volume of component V . They calculate δ from the formula

$$\delta = \sqrt{e} = \left(\frac{L_v - RT}{V} \right)^{1/2}$$

Determination of majority of values, entering this formula, does not present difficulties. Value L_v for many liquids at 25° can be calculated according to the equation, proposed by Hildebrand [11]:

$$L_v = 23,7T_k + 0,02T_k^2 - 2950$$

where T_k - absolute boiling point of liquid with 760 mm Hg.

Walker [9] considers it more correct to use for calculating heat of vaporization another formula:

$$L_v = 5075 + 3443 \cdot 10^{-3}t_k + 2299 \cdot 10^{-5}t_k^2 + 1262 \cdot 10^{-7}t_k^3$$

where t_k - boiling point of liquid, °C.

According to Walker's equation value L_v at 25° for benzene is equal to 8040 cal/mole while during its immediate determination is obtained 8175 cal/mole. Hildebrand's equation, δ is less accurately, since the difference between the experimental and

calculated values still more is approximately 300 cal/mole.

As a result of nonvolatility of polymers determination δ_n from heat of vaporization is impossible; therefore it is necessary to resort to indirect methods. Small [12] proposed to calculate this value, on the basis of the so-called molar coupling constants. Correlating numerous experimental data in the value of the pressure of vapors and heat of vaporization, Small established the effect of separate atomic groupings on the intensity of the reaction between the molecules (Table 2).

Page 50.

Value δ_n is calculated from formula [8]

$$\delta_n = \frac{\Sigma d}{M_0}$$

where Σd - sum of molar coupling constants of atomic groupings, entering monomer unit;

d - density;

M_0 - molecular weight of monomer.

Described method can be illustrated by following example. In polyacrylonitrile the repeating link is group $-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-$ molecular weight of which $M=53$.

Consequently

$$\Sigma d = 133 + 28 + 410 = 571 \quad \delta_n = \frac{571 \cdot 1.15}{53} = 12.4$$

Table 2. Molar coupling constants Γ [in (cal/cm²)^{1/2}] different atomic groupings at 25°.

Атомная группировка	(кал/см ²) ^{1/2}	Атомная группировка	(кал/см ²) ^{1/2}
—CH ₃	214	—H (подвижный)	80—100
>CH ₂	133	—O— (простые эфиры)	70
—CH	28	>C=O (кетонны)	275
—C—	—93	—C(=O)O— (сложные эфиры)	310
=CH ₂	190	—C≡N	410
—CH=	111	—Cl	270
=C=	19	—Cl в группировке >CCl ₂	260
H—C≡C—	285	—Cl в группировке —CCl ₃	250
—C≡C—	222	—Br	340
C ₆ H ₅ — (фенил)	735	—J	425
(o, m, p-) C ₆ H ₄ —	658	>CF ₂	150
(фенилен)		—CF ₃	274
C ₁₀ H ₇ — (нафтил)	1146	—S— (сульфиды)	215
C ₅ H ₉ — (пятичленное кольцо)	105—115	—SH (меркаптаны)	315
C ₆ H ₁₁ — (шестичленное кольцо)	95—105	—O—NO ₂ (нитраты)	~440
		—NO ₂ (алифатические соединения)	~440
		—PO ₄ (органические фосфаты)	~500

Key: (1). Atomic grouping. (2). (cal/cm²)^{1/2}. (3). mobile. (4). ethers. (5). ketones. (6). esters. (7). in grouping. (8). phenyl. (9). sulfides. (10). mercaptans. (11). naphthyl. (12). nitrates. (13). five-member. (14). aliphatic nitro-compounds. (15). six-membered ring. (16). organic phosphates.

Page 51.

Thus, solvents of polyacrylonitrile can be, apparently, substances, for which δ_p is within the limits from 10.9 to 13.9. Such substances include dimethyl formamide ($\delta_p = 12.1$), N-acetylpiperidine ($\delta_p = 11.5$), N-formylmorpholine ($\delta_p = 10.6$), chloroacetonitrile ($\delta_p = 12.4$). In all substances indicated polyacrylonitrile forms the concentrated

solutions, stable at room temperature. By a good solvency with respect to polyacrylonitrile are characterized also ethylene carbonate ($\delta_p=12,7$) and nitromethane ($\delta_p=12,2$).

However, there is series/number of cases, which contradict this theory. For example, for methylmalononitrile $\delta_p=11,8$, however this substance is not the solvent of polyacrylonitrile; for butyrolactone $\delta_p=14,5$, but it dissolves polyacrylonitrile. The dissolving effect of substances with the strongly associated molecules (for example, alcohols, phenols, unsubstituted and monosubstituted amides of carboxylic acids) is negligible. In the methyl alcohol, for which $\delta_p=13,4$, the polymer even will not swell. Nevertheless in many instances value δ_p is reference point during the selection of different solvents.

This method of calculation of solvency is applicable only of organic solvents; to solutions PAN in aqueous solutions of inorganic salts it is unsuitable.

Dimethyl formamide as the solvent of polyacrylonitrile.

At present as solvent of polyacrylonitrile dimethyl formamide (DMF) extensively is used.

Dimethyl formamide is comparatively high-boiling solvent (temp. b. p. of 152.5°); it mixes with water in every respect [13]. As a

result of the hygroscopicity DMF obtaining the solvent, which does not contain water, presents great technical difficulties; at the same time water, which is located in the solution PAN in the DMF, has a strong effect on the course of the technological process of obtaining the fiber.

Properties of concentrated solutions PAN in DMF are studied still little. Only in the works Houtz [14] and Hunyar [15] the separate stages of preparation of the spinning solution are examined and the data about the dependence of the viscosity/ductility/toughness of these solutions on molecular weight of polymer and its concentration in the solution are cited. Sonnerscog [16] investigated a change in the viscosity/ductility/toughness of the 18%-24 solutions in the dependence on the temperature; in the work of the Japanese researchers Katayama and Sakaba [17] the results of experiments regarding the viscosity of the solution with the different concentrations PAN in the DMF and at different temperatures were presented.

As a result of investigations, carried out in All-Union scientific research institute of synthetic fiber [18], it was established that concentrated solutions PAN in DMF are structured systems, degree of structuring depending, apparently, not only on value of molecular weight of polymer, but also on branching degree of chains of its macromolecules.

With increase of the concentration of polymer ($M=80000$) from 12 to 18% viscosity of the solution increase/grow more than 10 times (Fig. 8). They assume that so significant a structuring of the solution in the high degree is caused by the relatively high hardness of molecules PAN [19]. Viscosity of the solution PAN in the DMF virtually is not changed during the prolonged storage.

In view of the fact that DMF is hygroscopic, under production conditions it is sufficiently difficult to avoid complete drainage from spinning solution. And at the same time even small quantity of water considerably changes the properties of the solutions PAN in the DMF. Since water is coagulant for PAN, then in its presence in concentrated solutions their stability in the time is decreased, which is connected, most likely, with the formation of the grid of molecular bonds. Fig. 9 gives the results of the analyses of the effect of water in the dimethyl formamide solutions PAN on their viscosity/ductility/toughness [18]. The stability of solution was characterized by the ratio of the absolute viscosity of solution after its standing during 22 hour (η_{22}) to the viscosity/ductility/toughness of freshly prepared solution (η_0). As can be seen from given data, the effect of water on the stability of solutions the greater, the higher polymer concentration in the solution.

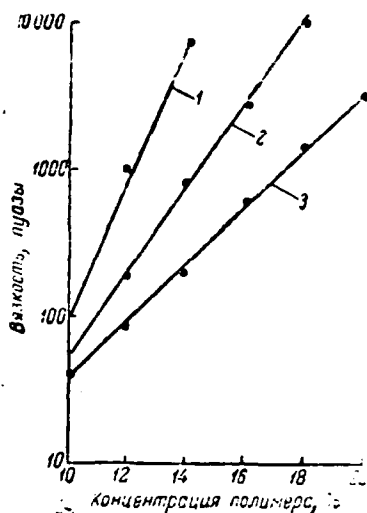


Fig. 8.

Fig. 8. Effect of polymer concentration on viscosity of the solution in different solvents: 1 - in solution $Mg(ClO_4)_2$; 2 - in solution $NaCNS$; 3 - in DMF.

Key: (1). viscosity, poise. (2). Polymer concentration, %

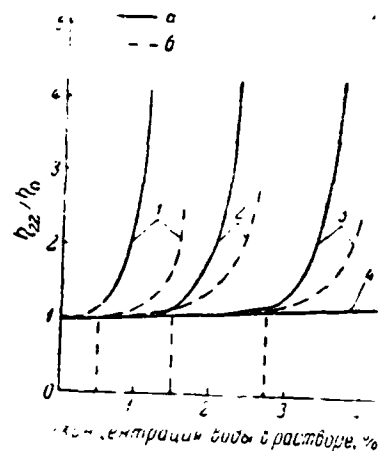


Fig. 9.

Fig. 9. The effect of the liquid-water content in the dimethyl formamide solution of polymer on the stability of the solution: a) with the shear stress 500 dn/cm^2 ; b) with the shear stress 8000 dn/cm^2 ; 1 - concentration of polymer 18% weight; 2 - the same 16% of weight; 3 - the same 14% of weight; 4 - the same 12% weight.

Key: (1) water concentration in the solution, %.

Page 53.

For obtaining the highly concentrated solutions PAN in the DMF, necessary for the dry spinning, it is possible to use only anhydrous solvent. During the dissolution of polymer with different molecular weight (with the equal concentrations of solutions and their equal

stability) in the solutions must be contained the less the water, the higher molecular weight of polymer. In practice for obtaining good spinning solutions polyacrylonitrile dissolve in the DMF, which contains not more than 0.5% water. With an increase of the quantity of water in the DMF its solvency is lowered, and for the complete dissolution PAN it is necessary to increase the temperature of dissolution [20].

Are cited below data about dependence of temperature of dissolution PAN in DMF on liquid-water content in solvent:

1) Содержание воды, % от веса раствора	0	1	2	3	4
2) Температура растворения, °C	-10	10-20	50-60	60-70	80-90

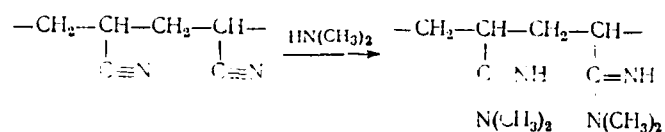
Key: (1). Liquid- water content, % from the weight of solution.

(2). Temperature of dissolution, °C.

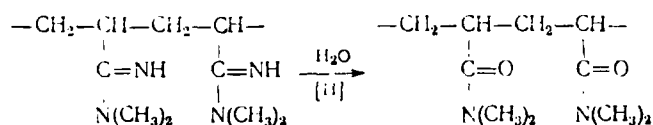
For decreasing coagulating effect/action of water was proposed to introduce into spinning solution dispersing agents in small quantities, for example compound of type of polyoxyethylated fatty acids or alkyl phenols [21], aldehydes, which relate to series/number of easily decomposed/expanded unsaturated ether-like/ester-like compounds [22], etc.

During heating viscosity of the solution considerably is reduced and effect of water on stability of solution is decreased. However, as a result of prolonged heating at temperatures of higher than 80° spinning solutions darken and the greater they are, the more it is contained in the solution of water. This phenomenon is connected with

the formation as a result of the hydrolysis DMF of a small quantity of dimethylamine. During the reaction of amines with polyacrylonitrile [23] are obtained the amidine compounds:



Under the effect of acid that painted of compound easily is saponified with formation of amides:



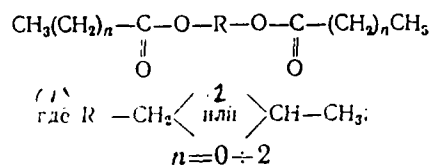
Intensity of coloring is reduced after addition to solution of strong acids (sulfuric, salt/hydrochloric) [24].

Page 54.

In presence of some substances of acid character (formic, nitric and some other acids), which generate with dimethylamine and ammonia of easily decomposed/expanded compound, spinning solution also it is stained. In the majority of the cases the darkening of the spinning solution even during the prolonged heating can be avoided by the introduction to it of different acid compounds. Usually to the spinning solution add about 0.5% of oxalic acid [25]; is proposed to also introduce the anhydrides of some mineral acids, for example SO_2 and CO_2 [23, 26], saturating by them the solvent before the

dissolution of polymer or passing through the solution in the process of dissolution; is recommended also to add into the solvent to 2% of weight of the anhydride of organic acid, the mixed with an equal quantity thiol (mercaptan), for example the mixture of succinic or acetic anhydride with 1- thioglycerin $\text{CH}_2\text{OHCHOHCH}_2\text{SH}$, 1.3-dithioglycerin $\text{CH}_2\text{SHCHOHCH}_2\text{SH}$, thiosorbitol [27], etc. For preventing the darkening of spinning solutions and obtaining of white fiber it is proposed also to add from 0.2 to 4% of weight of the mixture of sulfuric acid and organic sulfonic acid [28], 0.25% of weight of rongalite or 0.2% of weight of thiocyanate sodium [29].

Besides stabilizers of color value indicated, it is possible to add solvent diesters of general formula:



Key: (1). where. (2). or.

Polyacrylonitrile fiber obtained in this case has white color [30].

During heating of concentrated solutions PAN in DMF up to 100° and their cooling to room temperature reversible changes in properties of solutions occur. However, during the heating higher than 150° continues the irreversible process of gel formation, which is

accompanied by splitting and formation of three-dimensional structures [31]. Simultaneously at elevated temperatures of DMF it is decomposed/expanded with the splitting of dimethylamine, which, interacting with polyacrylonitrile, forms poly-amidine compounds [23]. The presence of comparatively reactive azine groups, connected with the polymer chain, conditions the ease/lightness of the formation of three-dimensional structures. The spinning solution PAN in the DMF is most stable at 50—70°. Usually, if 60000 use polymer with molecular weight of 80000, they form fiber from 15-17% solutions.

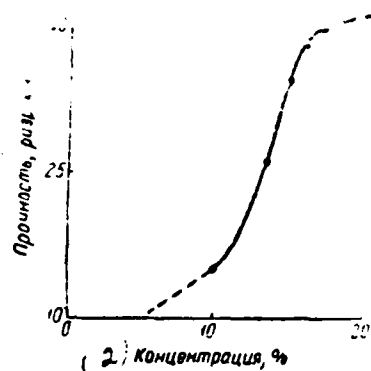


Fig. 10. Effect of polymer concentration in solution on strength of fiber.

Key: (1). Strength, razr. km. [breaking (razryvnoy) kilometer?] (2). Concentration, %.

Page 55.

Fig. 10 gives the experimental data, which show that with the concentrations of spinning solution, which exceed 17%, tensile strength of fiber increases/grows insignificantly. Moreover, it is necessary to have in mind that with an increase in the concentration the viscosity of the solution considerably is increased, as a result of which the processes of filtration and deairing of solutions hinder.

Quality of polyacrylonitrile fiber to a considerable extent depends on method of preparation of the spinning solution. A good fiber can be obtained only from the homogeneous, well filtering spinning solution, which does not contain gel-like particles and air bubbles. It is necessary to remember that the solubility of polyacrylonitrile depends not only on molecular weight of polymer, but

also on the method of its polymerization and drying regime.

Production process of dissolution PAN in a DMF.

In practice process of dissolution is conducted usually in two stages: during the first stage polymer they mix with solvent in cold; on the second - it is dissolved during heating [15, 25]. Preparation of concentrated solutions, polymers, used for spinning, a comparatively prolonged process. The basic stages of this process are: dissolution, filtration, deairing (removal/distance of the air bubbles from the solution).

Fig. 11 gives fundamental flow chart of preparation of the spinning solution PAN in DMF. Dimethyl formamide (DMF) from measuring tank 1, and polymer from a bin-batcher 2 enter special apparatus-mixer 3, where the uninterrupted mixing of dry DMF, undertaken in the necessary quantity, with polyacrylonitrile, occurs. In this case the suspension of polymer in the solvent is formed. The process of the dispersion of polymer in the solvent lasts from 30 min. to 1.5 hour. after obtaining of uniform mass suspension they pump through preheater 4 into the apparatus for dissolving (final solvent) 5, which is the tank, equipped with mixer and jacket for the heating. The process dissolving proceeds at 85-90°. For obtaining the uniform spinning solutions high value has the intensive mixing of both the suspension and the solution.

Deairing is most prolonged stage of process of preparation of the spinning solution. Air in the solution is located in the form of the small bubbles of different size/dimension, and also in the dissolved state. The solubility of gases in the solution depends on chemical nature of gases and solvent, and also on temperature and pressure.

Page 56.

Table 3 gives the absorption coefficients α , which characterize the solubility of some gases in the water, acetone and dimethyl formamide.

Given data show that gases, which are contained in air, are dissolved in organic liquids considerably better than in water. Since the concentrated solutions of polymers are viscous liquids, the deairing of spinning solutions is very hindered/hampered. These difficulties are aggravated even and by the fact that in the organic liquids the gases are inclined to form the supersaturated solutions.

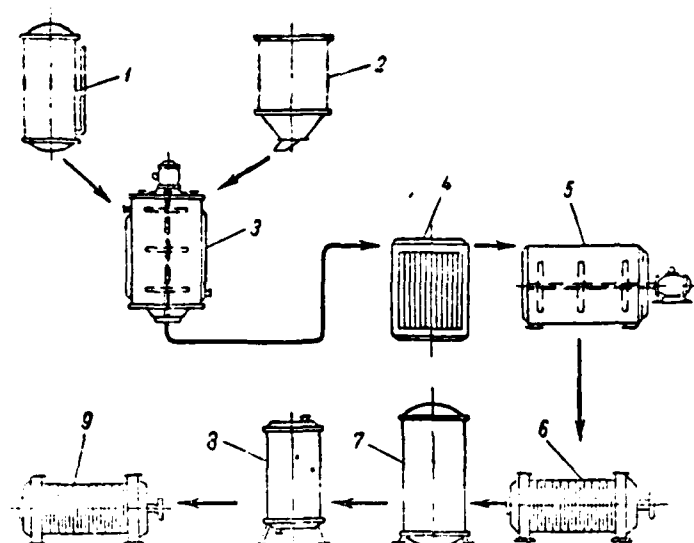


Fig. 11. Flow chart of obtaining spinning solution: 1 - measuring tank of dimethyl formamide; 2 - bin batcher of polymer; 3 - mixer; 4 - preheater; 5 - final solvent; 6 - filter press of first filtration; 7 - spinning tank; 8 - continuous evacuator; 9 - filter press of second filtration.

Table 3. Absorption coefficients of some gases by different solvents.

Газ	Коэффициенты абсорбции α		
	(3) водой	(4) ацетоном	(5) диметил- формами- дом
Азот	0,0143	—	0,0400
Кислород	0,0283	0,1940	0,1100
Оксись углерода	0,0214	—	0,0612
Углекислый газ	0,7590	—	0,4103

Key: (1). Gas. (2). Absorption coefficients α . (3). By water. (4). by acetone. (5). by dimethyl formamide. (6). Nitrogen. (7). Oxygen. (8). Carbon monoxide. (9). Carbon dioxide.

The removal of bubbles from the spinning solution can be accelerated while conducting of entire process of dissolution (beginning from the suspension of polymer) in the vacuum.

In process of preparation of the spinning solution in vacuum from solution all gases (dissolved and distributed in liquid in the form of small bubbles) are removed. The uninterrupted evacuation of spinning solution provides complete deairing, as a result of this the break of elementary fibrils during the molding is prevented.

Spinning solution must not contain not only bubbles of air, but also mechanical pollution/contamination. For removal of them solution from final solvent 5 supplies through the filter press 6 first filtration in the spinning tank 7, which serves as intermediate capacity. The filtered spinning solution does not contain mechanical pollution/contamination, or swollen, undissolved small pieces of polymer. They filter solution under the pressure to 10-12 atu through the dense cotton fabric and the cotton wool. For the final release from air and the mechanical pollution/contamination spinning solution they pass through the special apparatus - continuous evacuator 8, and then through the filter press of second filtration 9, after which they direct solution to the spinning. All communications, on which is passed the spinning solution, must be equipped with the special jackets, intended for the heating of solution by hot water. Filter presses also warm by the hot water, which circulates along the special

channels of frames and plates/slabs. Rate of filtration usually composes 20-30 l/m². . . The temperature of spinning solution is maintained in the range from 50 to 80°.

There is great technological interest in completely continuous process of preparation of the spinning solution. This process differs from that described above by the fact that the dissolution is conducted in continuous apparatuses, equipped with powerful/thick turbomixers.

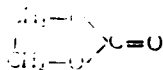
Other solvents of polyacrylonitrile.

Besides DMF, as solvent in production of polyacrylonitrile fibers is used dimethylacetamide (DMA) $\text{CH}_3\text{CON} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$; this liquid substance, which boils at 166°. Dimethylacetamide is somewhat less toxic than DMF; however, PAN in it is dissolved more badly than in DMF¹². Whereas in the DMF it is possible to obtain the solutions with the concentration approximately 30% of PAN, in DMA are obtained the solutions with the concentration not higher than 22%. DMA is capable to dissolve PAN only at a temperature higher than 70°; furthermore, it is more subjected to hydrolysis, than DMF therefore the fiber, which is obtained during molding of the solutions PAN in DMA, is colored yellow-brown.

Page 58.

Among nonvolatile organic matter, which found use as solvents for

PAN. should be named/called ethylene carbonate



and also its aqueous solution, which contains is more than 85% ethylene carbonate. The stability of ethylene-carbonate solutions and their spinnability are improved during the addition to them from 0.2 to 1.0% of ethylene glycol or salicylic acid. Nevertheless the solvency of ethylene-carbonate solutions is lower than DMF. The maximum concentration of polymer in this solvent does not exceed 20%. Usually the working concentration of the spinning solution PAN in EK composes 14-16%. Dissolution occurs during the heating to 95-100° [33].

Since ethylene carbonate boils at 238°. It cannot be used for obtaining the fiber with the dry method.

However, because of ease/lightness of its washout from fiber this solvent is very convenient in obtaining of fiber with wet process; furthermore, its large advantage is nontoxicity.

Very economically advantageous solvent can prove to be also dimethyl sulfoxide $(CH_3)_2SO$ - liquid with temp. 189°. Waste sulfite of lye serve as source material for its obtaining. The solutions of polyacrylonitrile in dimethyl sulfoxide are not virtually studied.

There is special interest in application as solvent PAN of concentrated solutions of some inorganic salts. Such salts are chloride and zinc bromide, thiocyanate salts of potassium, sodium, barium, calcium or magnesium, and also perchlorates of some metals.

Are of interest of analysis of salt solutions PAN of Hunyar and Grebe [35] and works of others scientists [36]. It was established that the viscosity of salt solutions PAN is not changed during several days, and also, that salt concentration in the water exerts a substantial influence on the viscosity/ductility/toughness of the equiconcentrated solutions PAN. Fig. 12 shows the dependence of the absolute viscosity 12% solution PAN on the composition of the dissolving mixture. From given data it is evident that there is a specific optimum of salt concentration, with which the solvency of salt solution is maximum, and the viscosity of the solution of polymer is minimum.

Further investigations [36] showed that polyacrylonitrile is dissolved not only in concentrated solutions of specific inorganic salts, but also in solutions of mixtures of some salts, moreover it seemed that "which dissolve" polyacrylonitrile, it is possible to partially replace with salts, "by those not dissolving" it, and to obtain "intensive-dissolving" salt mixtures.

Page 59.

Thus, the viscosity/ductility/toughness 12% solution PAN in the

solution, which contains 45% ZnCl_2 and 15% CaCl_2 , is 1.5 times lower than in 60% solution ZnCl_2 .

For spinning from salt solutions were proposed spinning solutions of different composition [37, 38], for example solutions, which contain 35.5% ZnCl_2 , 25.8% CaCl_2 and 38.7% H_2O . According to others data [39], the 20-25% solutions PAN can be obtained in the solvent, which contains, except water, 38-42% ZnCl_2 and 35-40% NH_4Cl .

However, for molding of polyacrylonitrile fiber it is inexpedient to use cut acid or its mixtures with other substances: first, due to very high viscosity of 10-12%- solutions of polymers and, secondly, due to absence of developed methods of complete regeneration of zinc salts. It is proposed to also obtain a PAN-fiber from the solutions PAN in the concentrated solutions of thiocyanate sodium. Solutions obtained in this case are very stable. In contrast to the process of the dissolution of polyacrylonitrile into the DMF, which takes place at a temperature lower than 100° , in the concentrated salt solutions PAN it is dissolved frequently during the heating up to 110° and it is above [34]. The difficulties of the preparation of the solutions PAN in the salt solutions consist also in the foaming and the poor deairing of viscous solutions [34].

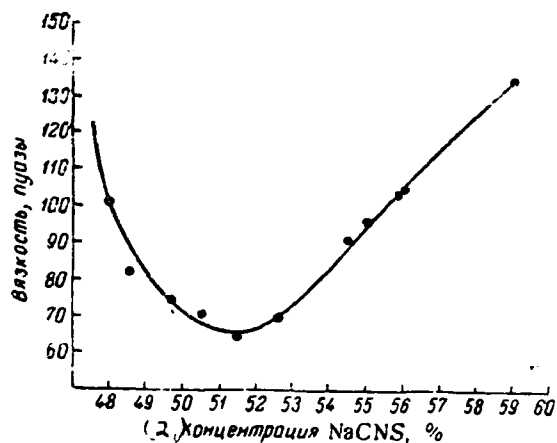


Fig. 12. Effect of composition of dissolving mixture salt - water on viscosity ductility/toughness 12% solution of polymer.

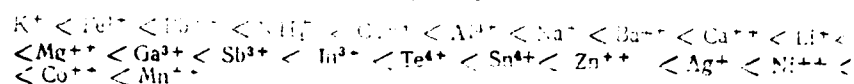
Key: (1). viscosity/ductility/toughness, poise. (2). Concentration NaCNS, %.

Page 60.

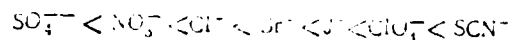
It is necessary to note that, in spite of comparatively high temperature of dissolution, polyacrylonitrile forms transparent, bright solutions, which indicates absence of chemical changes in macromolecule. In this one of the advantages of the utilization of aqueous solutions of some salts as the solvents consists.

Many hygroscopic salts possess dissolving effect/action with respect to polyacrylonitrile. Table 4 gives the characteristics of the solvency of salts. Cations and the anions of some salts it is possible to arrange in the order of the increasing capacity of the solutions of salts, formed by these ions, to dissolve PAN [37]:

Катионы



Анионы



Key: (1). Cations. (2). Anions.

Table 4. The solvency of the solutions of different inorganic salts with respect to PAN.

Анионы	Катионы										
	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺	Ag ⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺	Zn ²⁺	Cd ²⁺	Al ³⁺
SCN ⁻	+	+	+	+	-	+	+	+	+	+	+
ClO ₄ ⁻	+	+	+	-	-	+	+	+	+	+	+
J ⁻	+	+	-	-	-	+	+	+	+	-	+
Br ⁻	+	+	-	-	-	+	+	-	+	-	+
Cl ⁻	-	-	-	-	-	+	-	-	+	-	+
NO ₃ ⁻	-	-	-	-	+	-	-	-	-	-	+
SO ₄ ²⁻	-	-	-	-	-	-	-	-	-	-	-

Анионы	Катионы									
	Ga ³⁺	In ³⁺	Te ⁴⁺	In ⁴⁺	Ni ²⁺	Sb ³⁺	Pb ²⁺	Mn ²⁺	Fe ³⁺	Co ²⁺
SCN ⁻	+	+	+	+	+	+	+	+	+	+
ClO ₄ ⁻	+	+	+	+	+	+	+	+	+	+
J ⁻	+	+	+	+	+	-	+	-	+	+
Br ⁻	+	+	+	+	+	-	+	-	+	+
Cl ⁻	+	+	+	+	+	-	+	-	+	+
NO ₃ ⁻	-	-	-	+	-	-	+	+	+	+
SO ₄ ²⁻	-	-	-	-	-	-	-	-	-	-

(Conventional designations: + good solvency; - poor solvency).

Key: (1). Anions. (2). Cations.

Page 61.

Salts, whose solutions dissolve well PAN, are antimony chloride, zinc, nickel and manganese, and also halides, thiocyanates and

perchlorates of many metals; solutions of sulfates do dissolve PAN.

In selection of solvent it is necessary to consider not only its technical and economic characteristics (cost/value, accessibility, harmlessness), but also spinning conditions of obtained solutions of polymer. Under the normal conditions of spinning using the wet and dry method the solutions of polyacrylonitrile are not always formed. For example, Ham [40] indicates that the individual solvents or their mixtures do not form the solutions, which are formed using the water/aqueous method, if in the molecule are contained nitrocyano-, lactone- and anhydrous groups. In such cases the spinning is possible only using the dry method or on the wet with the application of organic baths. Exception is dioxane; the solutions PAN in this solvent can be formed in the water/aqueous bath. The solutions of polyacrylonitrile in the solvents, which contain dimethylcarbamide, cyclic carbonate, phosphite and dimethylamidophosphate groups, are formed well in the aqueous solutions. Apparently, different spinnability of solutions PAN is connected with the value of surface tension and with the structure of concentrated solutions.

However, principle of technology of preparation of the spinning solution in all cases one and the same (independent of type of selected solvent), although it is necessary to select appropriate type of apparatus and materials for its preparation/manufacture.

Page 62.

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Page 63.

Chapter 5.

SPINNING.

General principles of molding polyacrylonitrile fiber.

Process of spinning from spinning solutions of polyacrylonitrile (PAN) and its copolymers differs from process of molding other synthetic fibers - viscose, acetate or caproic. This is connected with the fact that polyacrylonitrile ¹ is dissolved in the limited number of solvents and under the normal conditions is not melted; the substances, in which the polymer is dissolved, little they are volatile or completely nonvolatile.

FOOTNOTE ¹. Since the dissolution of polyacrylonitrile, its copolymers, which contain is more than 90% acrylonitrile, and the mixtures, which contain not less than 50% PAN, and also spinning of them occurs in essence equally, subsequently will be described molding and the aftertreatment of the fiber from PAN. If during the application of copolymers or mixtures the need for any technological changes arises, these changes it will be specially stipulated.

ENDFOOTNOTE.

Majority of them is characterized by hydrophilic behavior, they easily mix with the water in every respect, while polymer itself virtually

does not join water. Therefore the common methods of molding chemically fibers - from acetone or alcohol in the water/aqueous baths, from the volatile solvents in hot air, from the molten state - for the production of polyacrylonitrile fiber are unsuitable.

In practice for spinning from spinning solution PAN are used "water/aqueous" method, method of molding in organic baths, method of dry spinning and method of molding from softened state (which is accomplished/realized under large pressure).

Spinning from fusion/melt PAN under normal conditions is impossible, since PAN and its copolymers during heating are not softened and, without being melted, they are decomposed/expanded with 280-300°. Only in the case of applying copolymers with high content of second monomer or addition to polymer of large quantity of plasticizer [1] softening temperature of polymer so it is lowered that becomes possible its molding under large pressure from softened state in the same manner, as molding monofilament.

Page 64.

But during the addition of large quantities of plasticizer or the application of fusible copolymers the physicomechanical properties of fiber deteriorate. Therefore in this book the spinning of PAN-fiber from the softened state is not described.

As has already been indicated, polyacrylonitrile is dissolved (in

cold or with heating) in dimethyl formamide (DMF), dimethylacetamide (DMA), concentrated solutions of some inorganic salts (for example, zinc chloride, thiocyanate sodium or of calcium, lithium chloride, etc.), in aqueous solution of ethylene carbonate (EK), acetonitrile, aqueous solution of nitro-methane, etc. In the production of fiber from PAN as the solvents were proposed DMF and DMA, the concentrated solutions of salts of zinc or some thiocyanates, the aqueous solution of ethylene carbonate, etc.

Solvent is selected not only depending on its cost/value of accessibility, but, as it was described above, and depending on spinning conditions of fiber. Thus, during the selection of solvent one should consider, what spinnerets will be used for spinning, i.e., how many fibrils will be simultaneously molded from the spinneret. Since in the production to use the dissimilar methods of spinning, should be used the varied conditions of landing.

During utilization as solvent of alkyl derived amides, i.e., DMF and DMA, it is possible to use for molding water/aqueous or organic baths, and also dry spreading method. In this case it is necessary to consider high temperature of boiling of DMF and DMA and pronounced hydrophobicity of polymer.

Water/aqueous precipitation baths, common for hydrophilic polymers, are barely suitable for molding of spinning solutions PAN in DMF or in DMA. Both solvents rapidly and in any relationships/ratios

mix with the water: DMF (and apparently, DMA) forms strong/durable hydrates with the water. Therefore with the extrusion of the spinning solution through the spinneret orifices solvent immediately mixes with the precipitation tank. After solvent elimination from the stream of spinning solution the polymer, which in the water barely will swell, immediately is upset in the unswollen state, as a result of which the fiber is brittle and brittle. This fiber, differing sometimes in terms of high tensile strength, has low wear resistance, and also low tensile strength "with the loop" or "with the knot". Therefore the spinning solutions of PAN in DMF or in DMA it is inexpedient to mold in the pure water or in the precipitation bath, which contains the large excess of the water, not connected with the added into the bath of DMF or DMA.

Page 65.

Only with such concentrations of these solvents in the water/aqueous precipitation bath, when a quantity of "open" water, not connected with DMF or DMA, small or when there is no "open" water generally in the precipitation bath, is obtained the fiber, sufficiently soft and strong/durable for the abrasion. In these cases molding actually occurs not in the water, while in the "organic" since the water entire/all or almost entire/all it is connected with DMF or DMA in the form of hydrates.

Organic precipitation baths comprise from specific organic solvents with addition of DMF or DMA. DMF and DMA easily mix with

many organic solvents, especially with the solvents of polar character, for example with highest alcohols (glycerin, etc.) or with the fatty acids. Solubility of DMF and DMA in the polyalcohols and other polar solvents is less than in the water, and therefore for the molding are suitable the organic baths, which contain a smaller quantity of DMF and DMA.

Fiber, molded in organic precipitation baths, does not have deficiencies, which fiber, molded in water/aqueous bath, possesses. However, organic precipitation baths have other deficiencies; so, they are dearer cost and regeneration of DMF and DMA from them is hindered/hampered.

Molding polyacrylonitrile fiber in dry method differs from molding in the same method of acetate or chloroacetic fiber. This is connected with the fact that acetone and other generally accepted solvents vaporize completely at 50-70°, while DMF and DMA as a result of the high boiling point are removed from the solution only at 150° and higher temperature. As a result of the need of increasing the temperature of spinning up to 150° during the dry molding of polyacrylonitrile the fiber from the solutions DMF or DMA strongly is complicated equipment of forming of the process of molding. Furthermore, it is known that the dry method of spinning is unsuitable for molding staple fiber, if a number of simultaneously molded fibers in one spinneret exceeds 100-200, since solvent does not manage to be vaporized with the surface of all streams and the part of the holes in

the spinneret it is closed up by spinning solution. Therefore the uninterrupted molding of spinning solution using the dry method possibly only in the production of filament thread or with the spinning of small staple it is flagellate.

During application as solvents PAN of aqueous solutions of salts (zinc chloride, thiocyanate sodium) or ethylene carbonate it is necessary to consider that only concentrated solutions of these substances in water (60-65% of zinc salt or 80-85% of ethylene carbonate) are capable of dissolving PAN; in both cases water, apparently, must be connected. For spinning from the spinning solutions PAN in the concentrated solutions of salts as the precipitation baths are used the solutions of the same salts, but containing only 50-55% salts; for spinning of fiber from the spinning solutions PAN in the aqueous solution EK the precipitation baths, which contain about 15-20% EK, are used.

Page 66.

Only in these cases it is possible to obtain the fiber, sufficiently strong/durable to the abrasion.

Method of spinning in organic baths, and also dry method of spinning are not used with spinning from PAN in such cases, when spinning solution PAN is prepared in aqueous solutions of salts or EK.

Molding of polyacrylonitrile fiber in water/aqueous precipitation

baths.

Spinning conditions of spinning solutions PAN in water or in mixture of water with solvents depend on "dissolving force" of solvent [2] (see Chapter 4).

Capacity of spinning solutions to form fibers in water/aqueous precipitation bath is determined by character of functional groups, which are contained in molecule of solvent. Thus, if in the molecule of solvent are dimethylcarbamide, cyclocarbonate or dimethylamidophosphate groups, then from the spinning solution PAN with its spinning out into the water or into the mixture of water with the solvent fibers are formed. If in the molecule of solvent are nitro-, cyano-, anhydrous or lactonic groups, then for spinning from the same solutions PAN it is not possible to use water/aqueous precipitation bath, and spinning can be conducted only in the organic baths or dryly.

For spinning in water/aqueous baths as solvents PAN are suitable, besides DMF, DMA and EK, also solutions of inorganic salts with strongly hydrated ions (salt of zinc, calcium, thiocyanates, haloids, etc.), and also dimethylsulfone, dioxane, dimethylphosphite, three (dimethylamido) phosphate, etc.

DMF and DMA acquired practical value as solvents, and recently also EK and concentrated solvents of sodium thiocyanate. In all these

cases the fiber is molded according to one and the same diagram. The concentrated spinning solution after its obtaining, filtration and deairing is heated for reduction in viscosity/ductility and increase of spinnability of solution, moreover polymer concentration in the spinning solution must be highest possible. Depending on the quality of polymer it is possible to obtain the solutions of polymer in DMF or DMA with the concentration to 190-220 g/l; in the aqueous solutions EK can be contained to 140-150 g/l of polymer, in the concentrated solutions of inorganic salts to 160 g/l¹.

FOOTNOTE ¹. In such cases, when instead of PAN its copolymers with vinyl acetate, methylmethacrylate, vinylpyridine, etc. are used, the content of polymer in the solution it is possible to increase, since the solubility of these copolymers in proportion to the decrease of the structure regularity of macromolecules is raised. ENDFOOTNOTE.

Page 67.

Concentration of PAN in the spinning solution must be increased not only from the economic consideration, but also in view of the fact that in this case the conditions of spinning and the quality of the obtained fiber are improved. Thus, with the spinning in the water 8% solution PAN in DMF is obtained very weak fiber; with an increase in the concentration of PAN to 10% strength of fiber is increased to 15 breaking km; with an increase in the concentration to 15% strength is increased to 35 breaking km; with the concentration PAN 17% strength is equal to 39 breaking km; with 19% - reaches 40-42 breaking km.

However, solutions with high concentration of PAN, suitable for production fibers, can be obtained only from polymer, which possesses low specific viscosity, since concentrated solution of polymer, which has high specific viscosity, very bindings and badly/poorly is spun. Furthermore, polymer must be characterized by uniform structure and good solubility. But on the other side, from the polymer, which possesses excessively low specific viscosity, cannot be spun filaments. For obtaining the sufficiently good fiber from the polymer PAN, which has average/mean specific viscosity, it not less than PAN, whereas of PAN with the higher high specific viscosity the same fiber is formed with spinning out 14% solution.

Concentration of polymer in spinning solution, and also properties of obtained fiber are determined even and by molecular weight of polymer [3]. The uninterrupted spinning of fiber is possible only during the utilization of a polymer with molecular weight [4] from 30,000 to 150,000. From the polymers with low molecular weight weak fiber is obtained; excessively high-molecular polymers also are spun with difficulty, and the quality of fiber is lowered, since polymer concentration in the spinning solution must be in this case lowered to 10%.

Temperature of spinning solution, which enters through spinneret orifices precipitation bath, has also high value; the higher temperature of spinning solution, the lower its viscosity/ductility

and the more uniform solution. Therefore frequently one should not only preheat solution during its obtaining, but additionally heat it to 110-120° in the spinning small pump or in spinneret [5].

Spinning set-up of solution PAN in different solvents in water/aqueous precipitation bath, which contains solvent, in principle is identical and in many respects resembles diagram of molding chloroine fiber in water-acetone bath. This diagram can be changed in the dependence on that, is spun filament thread (silk) either staple fiber with the finishing in cut form or in the braid (Fig. 13).

Data about molding of staple fiber from spinning solution PAN in DMF are cited below, since this method of obtaining staple fiber found widest of acceptances [6].

Page 68.

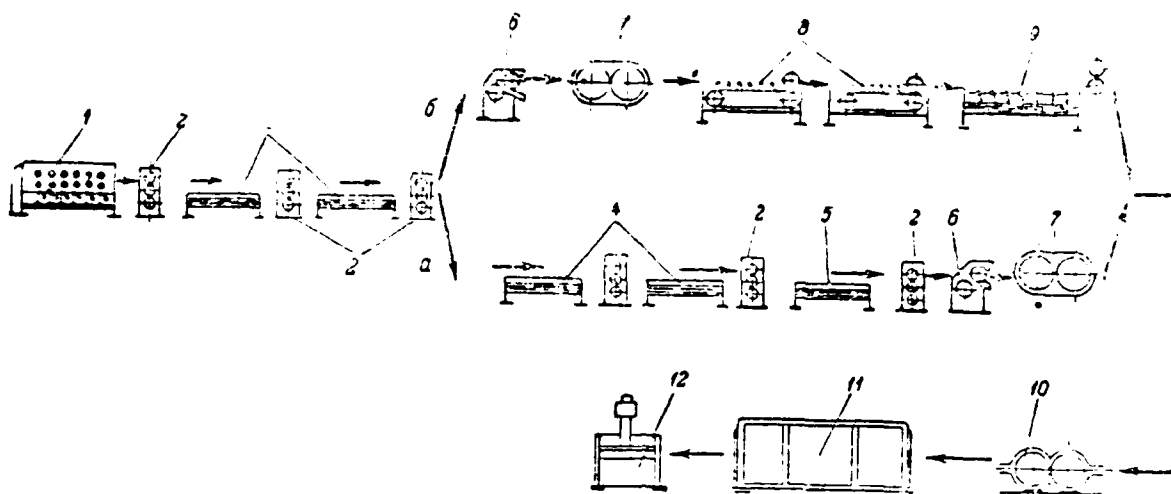


Fig. 13. Flow chart of obtaining nitronic fiber: a) finishing in braid; b) finishing in cut form. 1 - spinning machine; 2 - three-rolls; 3, 4 - exhaust baths; 5 - decoration bath; 6 - crimping machine tool; 7 - cutting braid; 8 - net machine; 9 - combing and soaping machine; 10 - loosener; 11 - dryer; 12 - baling press.

Page 69.

Spinning solution, which contains 16-18% PAN with viscosity/ductility 250-400 s. (on ball/sphere) and heated to 70-100°, they direct through spinning small pump into spinneret, and then into bath, which contains 30-60% DMF. Usually in the spinneret there are 3000-5000 holes, but their number can be still large, since in the water/aqueous precipitation bath sufficiently strong/durable fiber coagulates the spinning solution rapidly and in this case is formed. Experiment showed that the diameter of holes can be reduced from 0.1 to 0.08 mm without noticeable worsening/deterioration in the quality of fiber. With the decrease of the degree of die extract, i.e., the

decrease of size of holes in the spinneret. If spinning solution it is sufficient pure, the breakability of fibers during the spinning is reduced and spinning process becomes more stable. The bundle of fibers with the elementary number approximately 3000 most frequently is spun, but under the same conditions it is possible to spin fiber with the number to 6000. The speed of the passage of fibers in the precipitation bath is small - it does not exceed 2.0-5.0 m/min. The temperature of precipitation bath must be approximately 12-15°. At a temperature of bath of higher than 30° quality of fiber noticeably deteriorates (it is lowered extension at break). A decrease in the temperature of precipitation bath contributes to the best joining of "open water" with DMF (just as an increase in the content of DMF in the precipitation bath to 50-60%); however, to conduct process at 10° and below is economically inexpedient.

Depending on construction/design of spinning machine part bundle of fibers is passed to precipitation bath in horizontal or vertical direction from 0.5 to 3.0 m. It is experimentally established that spinning is completed at a distance of 0.2-0.5 m; with further increase of the way of thread in the bath the properties of the obtained fiber are changed little. This is explained by comparatively rigorous conditions of molding PAN-fiber in the water/aqueous precipitation bath. Actually fiber is completely molded at the very beginning of its passage in the precipitation bath, during 4-5 s.

Bundle of fibers, which emerges from precipitation bath, contains

about 300% DMF and about 160-200% of water from weight of PAN. This fiber possesses comparatively high tensile strength and small elongation. The multiplicity of drawing the freshly formed fiber depends on temperature. Cold fiber (at 20°) is pulled out 1.4-2.0 times (i.e. to 40-100%), in this case the sufficiently large effort of drawing is required. With an increase in the temperature of fiber to its 90-95° plasticity is raised: with the smaller effort/force the fiber can be pulled out to 700-800%. With an increase in the degree of stretch the strength of fiber increases/grows to 30-44 breaking km, and elongation respectively reaches 25-18%.

Page 70.

With an increase in the multiplicity of drawing (to a definite limit) the product of strength P by the elongation $l(P/l)$ and tensile strength of fiber with the loop are increased, and the elastic properties of fiber (it increases/grows a number of double bends) also are improved. With an increase in the multiplicity of drawing over the optimum value (to 6.0-9.0 depending on the properties of initial polymer) the strength is increased and elongation respectively is reduced, i.e., product P/l remains constant, and the elastic properties of fiber deteriorate.

Bundle of fibers is pulled out between two rollers or between three-rollers, arranged/located at a distance of 1.0-2.0 m from each other. For example, filament thread number 200 (40 monofilaments) they pull out between two heated rollers at 165-180° 10 times. i.e.,

to 300%; from the second rollers the thread is drawn down at a rate of 36 m/min. As a result the strength increases/grows from 5 to 40 breaking km; elongation composes 20% ($P_l=800$). With further increase in the extract the strength of thread can reach 44 breaking km during elongation 15%, but value P_l is decreased to 660.

Freshly formed bundle of fibers can be pulled out in hot bath (90-95°). In this case the fiber simultaneously is washed, and the content of DMF in it is reduced.

Extract sometimes is conducted into several steps/stages. Thus, the bundle of fibers immediately after outlet from the precipitation bath can be first extended between two godets to 40-50% in the cold state, then in the exhaust bath, which contains 10-20% DMF. After this, spinning factual is finished, and during further processing/treatment (hotter drawing, corrugation) the form of its cross section is not changed.

During utilization of other spinning solutions diagram of molding and conditions of drawing are not changed. If for the dissolution of polymer the concentrated solution of salts (for example, the solution, which contains 35% $ZnCl_2$, 25% $CaCl_2$, and 40% of water) is used, then precipitation bath must be the less concentrated solution of the same salts. The dilution of bath by water must be insignificant so that the conditions of spinning would be more moderated and fiber was soft. To dissolve polymer in the salt solutions is expedient at 100-120°.

For obtaining the soft fiber its molding in the precipitation bath should be conducted at a temperature not higher than 20°.

There was proposed [8] to decrease concentration of PAN in spinning solution to 7-8% and to mold fiber in pure water at temperature from 0 to +2°. In this case they pull out the freshly formed fiber in the tube (way of thread not less than 3.5-4.0 m) in the water at 98-100°. The multiplicity of extract is equal to 600%; drawing is produced between two godets.

Page 71.

The strength of thread is 40 breaking km during elongation 14%. If the fiber, spun from the salt solution, is preliminarily washed in the water, which has temperature of 10-35°, and only after this is subjected to extract, it is matte and rough. In the presence in the dissolving mixture besides ZnCl_2 , or SnCl_2 , also other less lyophilic salts (for example, CaCl_2 and NaCl) the solubility of PAN is improved, spinning conditions become softer and fiber is more elastic. The general/common content of salts in the dissolving mixture must compose 60-65%.

There are data, that in presence CaCl_2 , $\text{Ca}(\text{OCOCH}_3)_2$ and other salts in water-dimethylformamide precipitation bath spinning conditions also are softened and fiber is more elastic. However, when, in the precipitation bath, inorganic salts are present, its regeneration considerably is complicated.

For greater softening of spinning conditions of PAN-fiber from DMF-solutions it was proposed to conduct process in funnels with extract, used with spinning according to cuprammonium methods [9]. In this case of common 17% the spinning solution is spun through the spinneret with 50 holes (diameter of each hole 0.3 mm) into the soft water, which contains DMF. About 1 cm of way by air for vaporizing of part of DMF preliminarily pass the bundle of fibers. Thread goes out from the funnel with a velocity of 190 m/min and is accepted to the spool. After this, the freshly spun fiber is pulled out in the hot water at 90-95°ⁱⁿ 2.5-5.0 times; its strength in this case increases/grows to 35 breaking km during elongation 13%. The spinning speed of fiber taking into account extract reaches 500-600 m/min. The water, which contains significant quantities of DMF, continuously circulates through the funnel and partially it is directed to regeneration of DMF.

Thus, spinning from spinning solutions of PAN in water or in aqueous solutions of different solvents flows/occurs very rapidly. The more rapidly the polymer from the solution is upset, the harder the generating fiber. Soft fiber is formed during the utilization as the precipitation baths of concentrated solutions (for example, 50% of aqueous solution of DMF or 50% of solution $ZnCl_2$), the coagulation of fiber occurring comparatively slowly, which is explained by the presence of a very small quantity of "open" water.

Equipment shaping of spinning process in all cases indicated is equal. With the spinning of filament thread (silk) common viscose bobbin spinning machines can be used, they are machine for the spinning of chloroine silk in the water-acetone bath, the machine for the uninterrupted spinning and the finishing with two sloping set cylinders.

Page 72.

With the spinning of staple fiber it is possible to use the machines, intended for the spinning of viscose or chloroine staple fiber. It is necessary to only have in mind that with the work with the mixtures of DMF and water or with concentrated solutions $ZnCl_2$, in the water all machine parts, which are contacted with the spinning solution or the precipitation tank, must be manufactured from the stainless steel. Furthermore, one should consider that the vapors of DMF and DMA are harmful for the health; therefore the troughs of precipitation bath must be closed, and machine is connected with the ventilation.

Molding polyacrylonitrile fiber in organic baths.

Described above molding of PAN-fiber in water/aqueous precipitation tank actually can be considered molding in nonaqueous baths, since content of "open" water in water/aqueous baths is brought to minimum. However, usually the organic baths are called such, which contain only organic liquids or their mixtures without the water. In the literature and in the patents a large number of such baths is

described. This is explained by the fact that DMF and DMA, being up to now basic solvents PAN, easily mix with a large number of organic liquids: with fatty/greasy alcohols, fatty acids, hydrocarbons, etc. Therefore as the organic precipitation bath the most different substances can be used. The greatest application obtained the glycerin and other polyatomic alcohols, spindle oil and other hydrocarbons, and also the molten fatty acids.

Fiber, molded in organic baths, in contrast to fiber, molded in water/aqueous baths, is characterized by high elasticity and softness. The strength of fiber with the loop reaches 60-70%, while strength with the loop of the fiber, molded in water-DMF-baths, at present do not exceed 52-55%.

In organic baths it is possible to mold only spinning solutions of polymers in DMF and DMA, since inorganic salts in majority of organic liquids are not dissolved. The diagram of spinning in the organic baths is usually analogous to the diagrams of spinning in the water/aqueous baths. But in contrast to the water/aqueous baths in the organic baths only a small quantity of substance, used for the dissolution of polymer (DMF or DMA), is contained, since the solubility of it usually is comparatively small.

During utilization of glycerine, isopropyl, butyl, hexanetriol baths into composition of bath for increasing elasticity of fiber and softening of effect/action of bath it is useful to introduce to 20%

DMF.

Page 73.

Upsetting effect/action of organic bath is stronger, the higher its hydrophilic behavior; therefore with increase in number of groups OH and COOH in precipitation liquid upsetting effect/action of bath increases/grows. Furthermore, the upsetting effect/action of alcohols and fatty acids is decreased with an increase of the number of C-atoms in the chain of their molecules. Therefore the glycerine bath is more than "rigid", than hexanetriol, whose effect/action is stronger than bath from synthetic fatty/greasy alcohols, obtained from oxidized paraffins. The upsetting effect/action of the highest fatty acids (for example, the molten stearic acid) is so weak which for accelerating the coagulation of thread is necessary to raise the temperature of spinning up to 100°.

From one and polyatomic alcohols greatest application obtained glycerin ($\text{CH}_2\text{OHCH}_2\text{OHCH}_2\text{OH}$), isopropyl or n-butyl alcohol [10], hexanetriol ($\text{CH}_2\text{OHCH}_2\text{CH}_2\text{CHOHCH}_2\text{CH}_2\text{OH}$), polyalkylene-glycols [11], etc. Were also tested synthetic fatty/greasy alcohols from $\text{C}_{12}\text{H}_{25}\text{OH}$ to $\text{C}_{18}\text{H}_{37}\text{OH}$, and also fractions of the synthetic fatty acids, which contain molecules with 7-9 atoms of carbon, with 10-16 or with 17-21 atoms of carbon. Glycerin commonly is used at a normal temperature; during the utilization as the precipitation bath of propyl and butyl alcohols bath also it is not necessary to preheat; hexanetriol, highest fatty/greasy alcohols and the fatty acids, whose coagulating

effect/action is decreased with an increase of the number of carbon atoms in the chain, must be heated [12] to 80-100°.

With increase in temperature of precipitation bath strength of fiber increases/grows and speed of its molding is increased. Microphotography/microphotographs showed that during molding of PAN-fiber in the organic baths from highest fatty acids or fatty/greasy alcohols at 20-30° microsection is increased. Only in the process of molding at 60° or above fiber acquires normal shear/section. Even better proved to be the property fibers, spun in the fattyalcohol baths at 100-110°. The same effect on the properties of the obtained fiber exerts an increase of the path length of thread in the bath. While with the landing in the glycerine bath it is possible to reduce the route segment of thread or to increase the spinning speed, in the fattyalcohol baths for obtaining the fiber with the same properties it is necessary to increase the path length of thread or to decrease the spinning speed.

Nonpolar hydrocarbons are weakest precipitants, since DMF in them little is soluble. Thus, the recently proposed method of molding PAN-fibers in kerosene bath [13] is based on heating of precipitation bath to 120-130°.

Page 74.

It was also proposed to use the spindle oil (mixture of paraffins with 19-20 atoms of carbon in the molecule), heated up to 130°, as the

precipitation bath. The necessary for spinning temperature of precipitation bath from the spindle oil can be reduced, if this oil is subjected to hydroxyethylation, i.e., we introduce into the molecules of paraffin hydroxyethyl groups $(-\text{CH}_2-\text{CH}_2-\text{O})_n$. For strengthening the effect/action of purely hydrocarbon baths it was proposed to introduce into their composition the chlorinated hydrocarbons (dichloroethane, methylene chloride, dichlorobenzene, etc.); however during the addition of these substances working conditions in the production deteriorate.

Everything said above relates to spinning solutions of PAN and DMF or DMA. During the utilization as solvent 88-92% of nitromethane in the mixture with 7-12% of water as precipitant can serve pure/clean nitromethane [14], heated to 70-90°, and also [14] toluene, xylene or any other aromatic hydrocarbon, heated up to 100°. Water as the precipitant in this case is unsuitable, since the solvent, whose molecules contain nitro group, badly/poorly mixes with the water.

During application as solvent 80-85% of aqueous solutions of EK as precipitation bath besides water can be used [15] also anhydrous glycerin, glycol and other alcohols at temperature from 0 to 5°.

Further processing/treatment of fiber, obtained in organic baths, differs little from processing/treatment of fiber, obtained in DMF-water/aqueous baths. In both cases the freshly formed fiber must be subjected to extract, after which it acquires good textile

properties.

Fiber, spun in water/aqueous baths, can be elongated to 40-100% in cold, since it contains to 300% DMF from weight of polymer. The fiber, obtained in the organic baths, usually can be elongated only in the heated state. Therefore it they pull out directly in the precipitation bath at 100-120°; the multiplicity of the extract of 5-6 times. The fiber, spun in the water/aqueous baths, during the subsequent extract after washing, i.e., in the process of finishing (which is described in the following section) in the hot water at 100° or at 160-170° in the medium of hot air or live steam, is pulled out in all to 700-900%. The fiber, obtained in the organic baths, in hot air or vapor can be pulled out to 1000-2000%, since as a result of the gradual coagulation of polymer it is more plastic.

Comparing fibers, obtained in precipitation baths of different composition, it is possible to conclude that in organic baths fiber must be softer and more elastic. However, with an increase in the content of DMF in the water/aqueous bath this difference in the properties of the obtained fiber is smoothed also in both types of bath equivalent fiber is obtained.

Page 75.

For obtaining the elastic and soft fiber in the glycerine or hexanetriol bath it is necessary, in order to in this bath, as in the water/aqueous, was contained the specific quantity of DMF, although it

can be less than in the water/aqueous baths. Apparently, to the hydrocarbon baths it is inexpedient to add other substances, which amplify the coagulating effect/action of precipitant. From the organic baths, most likely, most effective are glycerine, and also the baths, which contain hexanetriol, n-butyl or isopropyl alcohol, and other baths from the lowest mono or polyalcohols (for example, glycol bath).

Dry spreading method of PAN-fiber.

As has already been indicated, dry method of spinning from spinning solutions PAN can be used only for molding of silk thread and in such cases, when for dissolution volatile solvent was undertaken. Therefore the dry spinning are suitable only the solutions of PAN in DMF and to a lesser degree solutions of PAN and DMA or nitromethane.

In principle this method does not differ from known spreading method of rayon in spinning cells in medium of hot air, but technologically it proved to be considerably more complex. Basic difficulty is high boiling point of DMF (153°) and a small volatility of its vapors, in consequence of which the spinning solution does not manage to vaporize and during the extrusion of streams from the spinneret it easily flows to its adjacent holes. For an increase in the volatility of DMF it was proposed to add to the spinning solution PAN in DMF to 10-20% of cyclohexanone or any other diluent of spinning solution with the moderate volatility of vapors [16]. For preventing

the inflow of spinning solution it was recommended to cover/coat the lower surface of spinneret with the mixture of graphite and wax [17].

One of basic requirements for polymer with spinning of fiber PAN using dry method consists in the fact that polymer must have low molecular weight (not higher than 50 000), but its solution - small specific viscosity (not higher than 0.7 for 0.2% of solution).

Only of polymer with low molecular weight it is possible to obtain more concentrated spinning solution, which contains to 30% of polymer. This solution during the vaporization of solvent immediately hardens in the form of fiber and, consequently, the inflow of solution on it occurs.

Page 76.

To obtain polymer with low molecular weight is technologically sufficiently complicated, since reduction in molecular weight of polymer is usually conjugated with an increase in the molecular nonuniformity, which leads to worsening/deterioration in the conditions for the dissolution of polymer and reduction in the strength of the obtained fiber. Thus, only under the conditions of the high evenness of polymerization it is possible to obtain the polymer, suitable for the dry molding.

Obtained 26-30% spinning solution with viscosity/ductility approximately 600-800 s. (on ball/sphere) after its filtration and

deairing is heated additionally to 110-120° for reduction in viscosity/ductility and for facilitating passage through spinneret orifices. In the avoidance of the yellowing of the solution of PAN in DMF during the heating to it is added the stabilizer: oxalic acid, bisulfite, derivatives of formaldehyde, etc. [18].

Molding is produced in common spinning machine for dry spinning (Fig. 14), but with increased mine/shaft, which has the height more than 4 m. Mine/shaft is warmed outside (by electricity, by vapors of Dowtherm or by water high-pressure vapor at a temperature to 200-300°) so that air within the mine/shaft would be heated [19] to 165-180°. Through the mine/shaft with the definite speed air, heated to the same temperature, is sucked. The evaporating DMF is taken away by air for the regeneration. Spinning speed must be such that the emerging thread would take away not less than 2.5 and not more than 5.0% DMF from its weight, since only with this content of DMF thread is sufficiently plastic and suitable for its additional drawing in the hot state.

In contrast to methods of wet molding of PAN-fiber in water/aqueous either organic or organic baths, during dry molding process of formation of fiber is not finished in mine/shaft, since during passage through it fiber does not test/experience tension and molecule barely they are oriented. For imparting to fiber the required textile properties its strong extract in the heated state is necessary.

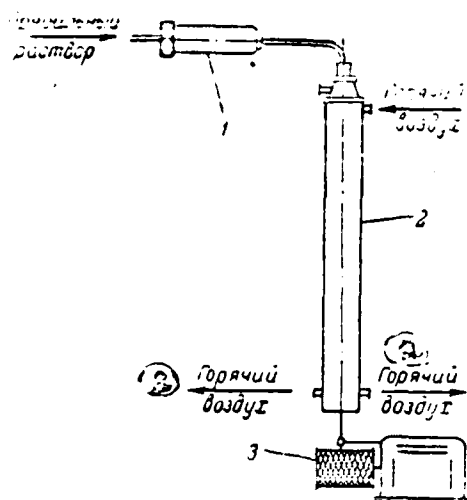


Fig. 14. Flow chart of obtaining nitronic fiber with dry method: 1 - bougie; 2 - spinning cell; 3 - mechanism of coil/winding.

Key: (1). Spinning solution. (2). Hot air.

Page 77.

This extract is accomplished/realized usually immediately after the outlet of the bundle of fibers from the mine/shaft, until they still contain a sufficient quantity of DMF or any other substance, which plasticizes polymer [20]. Fibers pull out between two rollers in the steam or air medium (at a maximum permissible temperature) 6-20 times (Fig. 15). The degree of stretch is greater, the higher the temperature, and also the more is contained plasticizer in the fiber. With an increase in the multiplicity of drawing (to the known limit - from 15 to the 22--fold) the quality of fiber is raised. Temperature can be raised also to a definite limit; with an excessive increase in the temperature the break of fiber and its yellowing is observed.

Besides DMF-solutions of PAN, for dry method of molding are suitable solutions of PAN in other amides of acids, in dinitriles, organic thiocyanates, in nitrile of glycollic acid, in N-cyclic compounds, in derivatives of pyrrolidone, pyridine, piperidine and other volatile compounds, which are capable of dissolving PAN with formation of spinning solutions, which contain not less than 15% polymer [21, 22].

In all cases after dry spinning undergoes 10-12--fold extract (into one or two steps/stages) and only after this it obtains necessary strength: 40-44 breaking km with extension at break of approximately 20%.

Regeneration of evaporating solvent has high value. Besides the common methods of the regeneration of DMF or other solvents, it was proposed to catch from the gas-air mixture the evaporating solvent directly in the spinning cell. For this the upper part of the mine/shaft is heated approximately up to 200°, and lower is cooled to 10-20°. Since the vapors of DMF are heavier than air, they lower in the mine/shaft downward. Coming into contact with the cold walls of the lower part of the mine/shaft, vapors are condensed and flow along the tubes/pipes in the form of liquid solvent. Thus it is possible to regenerate almost 100% DMF, but used this method should be only during the complete hermetic sealing of mine/shaft. Therefore with the frequent break of spinning, caused by the plugging of spinneret or by other reasons, this method of regeneration proves to be economically unfavorable as a result of the large losses of vapors of DMF with the opening of mine/shaft.

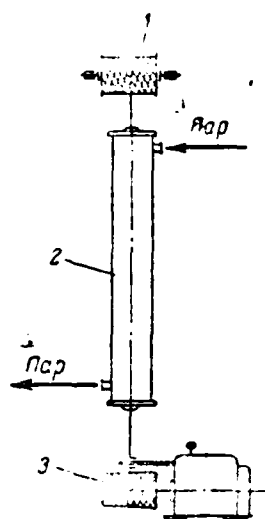


Fig. 15. Flow chart of hot drawing of the fiber in medium of live steam: 1 - spool with nonstretched fiber; 2 - tube/pipe for extract; 3 - receiving mechanism.

Key: (1). Vapor.

Page 78.

Effect of spinning conditions on the quality of fiber and the comparison of the different methods of molding PAN-fiber.

Among available numerous methods of spinning from polyacrylonitrile practical application found only following: molding spinning solutions of PAN in DMF (or in DMA) in water/aqueous and organic baths; molding from dry method; molding salt solutions in water-salt baths; molding spinning solutions PAN in EK in water-EK-solutions and in organic baths. Molding the spinning solutions in the nitromethane, in the acetonitrile and in other

solvents, the funnel method of molding the solutions of PAN in DMF, the molding of PAN in the softened state and others were, apparently, they were tested only under laboratory conditions or only proposed for the testing. Among the enumerated here virtually realized methods the widest use obtained the method of molding the solutions of PAN in DMF (or DMA), in the water and the organic solvents, and also molding using the dry method. Judging according to published data, dry method is used for molding of filament thread; the wet processes of molding are used in essence for the production of staple fiber.

One of most essential deficiencies in PAN-fiber is its brittleness and insufficient strength during abrasion. This deficiency, observed not only in the production of PAN-fiber, but also in the production of other synthetic fibers, is caused, apparently, by forming of strongly oriented dense dense surface layer. This layer is the reason for the low strength of fiber in the transverse direction (during the testing for break of thread with the loop or with the knot, during the abrasion, with the repeated bends and during other tests of the fibers, connected with the manifestation of the elastic properties of fiber in the transverse direction). The orientation layer is formed on the surface of synthetic fibers with the fast separation of polymer from the spinning solution; the more rapidly the polymer is separated/liberated, the denser the orientational layer and the more brittle fiber is obtained.

Polyacrylonitrile is strongly expressed hydrophobic polar

polymer. It is possible to dissolve it only in the strongly polar solvents. The majorities of these solvents interact with the water (DMF, DMA, EK, lyophilic salts, etc.), they easily are removed from the spinning solution into the coagulation bath, in which is contained the water or the compounds, which have the hydroxyl groups. With rapid withdrawal of solvent the polymer immediately is upset from the solution.

Page 79.

Therefore during the molding in the water or in the pure/clean hydroxyl-containing solvents PAN-fiber is brittle and unstable for the abrasion. Only during weakening of the effect/action of groups OH of water or alcohols, for example, by introduction to the composition of the bath of the solvent of polymer it is possible to weaken/attenuate the effect/action of coagulation bath and to obtain the fiber, strong/durable to the abrasion and possessing good elastic properties.

Because of high light resistance, good heat resistance, good elastic properties, looseness of pulp and "woolliness" the PAN-fiber is especially useful for application in mixture with wool or for its replacement in wool articles. Therefore wear resistance and high elasticity are very important qualities during the utilization of these fibers in the textile industry. As it was already indicated, the basic method of obtaining a similar high quality fiber is the application of "soft" baths, which do not contain "open" water or significant quantity of substances, into molecule of which enter the

"free" groups OH

With dry method of molding synthetic fibers orientational layer is formed so not rapidly and obtaining strong/durable for abrasion and elastomeric fibers is achieved via support in spinning cell of not too high temperatures or by addition to spinning solution of volatilizing with difficulty "plasticizer", for example nitriles of highest fatty acids.

Another serious deficiency in PAN-fiber is nonuniformity of its molecular structure: dissimilar density of arrangement, different flexibility of macromolecules, presence of micropores. Because of this are created dissimilar conditions for the diffusion of reagents into the depth of fiber, and also for dyeing/coloring PAN-fiber. Only during the molding under the softest conditions, and such with a strict constancy of mechanical stresses it is possible to obtain PAN-fiber, comparatively uniform according to the structure.

Other common defects of staple fibers: cementings, flys, dead fibers, roviness, etc. - in the production of PAN-fibers are encountered rarely and they can be easily eliminated, since PAN-fiber from the spinning solution is molded rapidly and coagulation is finished almost instantly.

Quality of PAN-fiber can be judged also from form of cross fiber section. This shear/section must have little cut or almost smooth

surface and must resemble on the form of dumbbell. The presence of the vacuums visible under the microscope in the cross section of fiber or the strongly cut form of shear/section testify about the too rigorous conditions of coagulation; circular shear/section - about the too soft conditions of coagulation.

Page 80.

Comparing different methods of molding of PAN-fiber, used on industrial scale, it is possible to arrive at conclusion that during utilization of water/aqueous method of molding PAN-fiber from DMF-solutions is not obtained this soft fiber (during testing of tensile strength with loop or with knot) as with spinning from the same spinning solution in organic baths, comprised of substances, whose molecules contain few groups OH. Only during the addition to the water/aqueous bath of the corresponding quantity of DMF (for example, with the water/aqueous spinning to 50-60% DMF from the composition of bath; during the application of a glycerin to 20% DMF) fiber differs little in the properties from the fibers, obtained in the baths, which contain fatty/greasy alcohols or molten fatty acids.

Apparently, it is inexpedient to use hydrocarbon baths in pure form (kerosene, spindle oil) or with additive of precipitants (for example, dichloroethane), since in this case regeneration of bath strongly is complicated, but quality of fiber is not improved.

Table 5 gives physicomechanical characteristics of fiber, molded

in different precipitation baths.

During estimation of different solvents and methods of molding of PAN-fiber it is possible to conclude following.

1. DMF is good solvent, and during its utilization fiber of good quality can be obtained, but it is toxic and it is comparatively expensive.

Table 5. Physicomechanical properties of the polyacrylonitrile staple fiber, obtained in different precipitation baths.

Осадительная ванна	Прочность разр., км	Удлине- ние, %	Относительная прочность в петле %	Число двойных изгибов	Усадка в кипящей воде %
(1) Вода + 50% ДМФ* при 20°	16—23	17—24	25—35	3 000—3 000	12—13
(2) Вода + 50% ДМФ* при 10°	20—25	22—30	40—50	14 000—18 000	7—9
(3) Гексантриол при 90°	10—13	15—23	15—20	15 000—16 000	5—6
(4) Жирные кислоты при 80°	20—28	26—33	45—60	16 000—19 000	5—9
(10) Вода + 55% NaCNS при 2°	18—20	17—20	30—45	10 000—14 000	8—12

Key: (1). Precipitation bath. (2). Strength, breaking km. (3). Elongation, %. (4). Relative loop strength %. (5). Number of double bends. (6). Contraction in boiling water %. (7). Water ... DMF ¹ with.

FOOTNOTE ¹. Copolymers fiber under otherwise equal conditions are molded more easily and "softer" than fiber from pure/clean PAN.

Therefore with spinning from the copolymers in the solution of DMF the water-DMF bath can have a temperature of 15-18° instead of 10-12°.

ENDFOOTNOTE.

(8). Hexanetriol at 90°. (9). Fatty acids at 80°. (10). Water +55% NaCNS at 2°.

Page 81.

It is most easy to regenerate vapors of DMF from the air-steam mixture with the dry method of molding (by freezeout method). With the water/aqueous method of molding, suitable only with the content of DMF

in the bath more than 40-50% and with the appropriate reduction in its temperature, for the regeneration of DMF a comparatively high steam consumption is required, since in the rectifying column from the DMF it is necessary to distill water vapors.

In the case of applying organic baths fiber is obtained more high quality. Such baths can consist of glycerin, isopropyl alcohol or glycol and must contain 15-25% DMF. Fiber in this case is high quality because of the slow coagulation of polymer from the spinning solution, but regeneration of DMF is complicated.

2. DMA, applied as solvent, differs little from DMF. In view of the smaller solvency of DMA the spinning speed must be lowered. This solvent is somewhat cheaper than DMF, but on the toxicity they, apparently, they are equivalent.

3. During utilization of concentrated solutions of salts, especially ZnCl_2 and CaCl_2 , processes of dissolution and molding are accompanied, apparently, by partial hydrolysis of PAN by formation of carbamide groups of type CONH_2 . Thus, actually is molded not PAN-fiber, but fiber from copolymer of acrylonitrile and small quantity of acrylamide. In the presence of carbamide groups dyeing/coloring fiber is facilitated, but somewhat deteriorate its physicomechanical and some textile properties. The process of molding proceeds easily, on the wear resistance of the obtained fiber it is lower than for the fiber from PAN, obtained by other methods. The

quality of fiber to a great degree depends on spinning conditions: temperature, the efforts/forces of drawing, salt concentration, etc., since at elevated temperatures the hydrolysis of groups CN of polymer to CONH₂ is feasible. In practice it is not always possible to obtain fibers of identical quality, especially with respect to the staining/coloring. The spinning speed of fiber also is reduced (in comparison with the speed with other methods of molding), since for the coagulation is used the bath, which differs little from the composition of the solution of salts, used for the dissolution of PAN. Solvent recovery is very simple - only expulsion of water from the precipitation bath is required.

4. EK as solvent is used at present only on experimental scale, but, judging according to published data, it can be of practical interest. This solvent is cheap and nontoxic. Its regeneration from the aqueous solutions is simple and is accomplished/realized in the vacuum evaporating apparatuses. However, there are data, which during the regeneration EK is partially hydrolyzed.

Page 82.

5. Concentrated solutions NaCNS in pure form or in mixture with Ca(CNS)₂ are capable of dissolving both monomer - acrylonitrile, and polymer - PAN and therefore they can be used for continuous polymerization, i.e., for direct obtaining of spinning solution from monomer. Obtaining copolymers is complicated by the fact that the speeds of the polymerization of different vinyl monomers in

concentrated solution NaCNS strongly are distinguished. In view of the high viscosity of spinning solutions of PAN and copolymers in concentrated solutions NaCNS it is necessary to decrease polymer concentration in the solution to 12% and less. Molding occurs easily, but regeneration NaCNS from the finished precipitation baths is connected with the organization of multistage vacuum evaporating installations. The quality of the obtained fiber, according to published data, is not inferior to the quality of the fiber, obtained from DMF-solutions.

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Page 83.

Chapter 6.

FINISHING.

General information about the decoration operations.

Usually by finishing are understood all operations, which are necessary for transforming freshly formed fiber into finished/prepared and are fulfilled at plants of synthetic fiber. In the production of nitronic staple fiber or silk such operations are the washing for the solvent elimination, bleaching for the removal/distance of the yellow hue of fiber, drawing of the fiber in the plastic state, imparting to it winding, drying and thermal stabilization of finished fiber (textile operations of twist and rewinding, and also the loosening of staple fiber in this book are not brought to light). The equipment shaping of decoration operations is dissimilar for the production of silk thread and staple fiber, it differently also with the aftertreatment of staple fibers in tow form and in cut form. But the essence of each of the enumerated operations in all cases remains identical.

Washing of nitronic fiber for the removal of the remainders/residues of solvent.

Depending on character and composition of solvent it is removed from fiber with different speed. The rate of washing depends on the

quantity of solvent, taken away by fiber from the precipitation bath and the distribution coefficient (K) of the solvent between the polymer and the water. Value K depends on the character of the groupings in the molecule of solvent and is decreased in the presence of the hydrophilic groups OH or COOH.

Therefore glycol, glycerin and other polyalcohols are washed clean more easily than alkyl-formamides. For DMF (according to experimental data) value K is equal to approximately 1, i.e., concentration of DMF in the fiber and in the water under the conditions of equilibrium is almost identical. For the poly-hydroxy compounds the concentration of solvent in the water is considerably higher than in the polymer, and, consequently, value K for these compounds is decreased.

Page 84.

Rate of washing of fiber on solvent depends not only on value of K but also on number of intermediate steps/stages of expressed substance of fiber between sections of decoration aggregate and on value of expressed substance, or on quantity of wash water and concentration of solvents in water.

With different value of distribution coefficient of solvent explained dissimilar carry-off of solvent by fiber from precipitation bath into wash. With the spinning of the solutions of PAN in DMF freshly spun fiber, which emerges from the precipitation bath, it

contained (depending on the spinning speed and composition of precipitation bath) by 250-300% DMF from the weight of polymer. For glycerine and other precipitation baths the percentage of the carry-off of solvent by fiber (according to published data) is lower and is decreased in proportion to worsening/deterioration in the dissolving force of precipitation bath. Knowing the content of solvent in the fiber and the distribution coefficient K , it is possible to calculate a number of washings of fiber [1], necessary so that the content of solvent in the fiber would not exceed 0.1%. Thus, calculation shows that for PAN-fiber, obtained from DMF of solutions, is sufficient 6-7 washings by hot water. For the economy of water and heat, and also for an increase in the content of solvent in the wash water removed by the regeneration is expedient to organize the countercurrent flow of water, i.e., the freshly formed fiber, which emerges from the precipitation bath, to wash in the used water, and fresh water to supply only for the final washing of DMF from the fiber. During the correct organization of the countercurrent flow of water it can be expended/consumed to 0.1 m³ on 1 kg. of fiber and less, and the content of DMF in the wash water it is possible to bring to 20-25% and more.

There are data [2], that washing of fiber is accelerated, and content of DMF in water is increased with use of water, heated to 85-90° and above. Even better results are obtained, if we wash clean nitronic staple fiber by power water, but this method of washing of DMF is hardly in practice advisable, since for its realization

autoclaves are required and during its utilization the continuity of work is disturbed. Furthermore, as a result of the strong contraction of cut staple fiber as a result of processing by its water in the autoclave the quality of fiber can considerably be lowered.

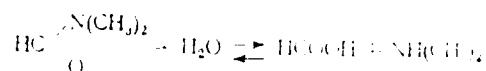
Practice established that to wash PAN-fiber, which contains DMF, is possible not only by hot, but also by cold water.

Page 85.

Bleaching of PAN-fiber.

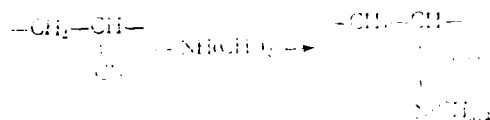
With molding of PAN-fiber from solutions in DMF or DMA it is slightly (and sometimes also considerably) painted in yellow. The conducted investigations showed that the yellowishness can appear as a result of the hydrolysis of initial solvent during the heating and due to the alkaline processing of finished fiber.

Hydrolysis of DMF and DMA at elevated temperatures (during rectification of solvent or during heating of spinning solution) flows/occurs according to diagram:



The catalyst of hydrolysis is usually the being present in DMF formic or in DMA acetic acid, which are formed as a result of thermal breakdown of DMF and DMA at high temperatures (for example, during the distillation of DMF at a normal pressure and 150-154°). The

dimethylamine separating with the hydrolysis enters with polyacrylonitrile in the reaction



with the formation of amidine groupings, that also conditions the appearance of brilliant yellow coloring. The same yellowing can occur in the case of formation as a result of the hydrolysis of any other primary or secondary amines or ammonia. But if hydrolysis is accompanied by the formation of tertiary amines, the staining/coloring of polymer does not occur, since the formation of amidine groups in this case is impossible.

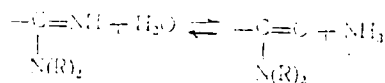
During processing/treatment of PAN-fiber by alkalis (even during processing/treatment by alkaline soap) or by power water, heated to high temperature, cyano--groups are also hydrolyzed [3]; in this case ammonia, which causes yellowing of fiber [4], is split off. Thus, and in this case the reason for yellowing is the formation of groups $>\text{C}=\text{NH}$. Furthermore, in the presence of alkalis, and also during heating of fiber can be formed cyclic di- or triazine groupings between the adjacent cyano-groups or the naphthidine structures, which also cause yellow staining/coloring.

To avoid yellowing of spinning solution or finished fiber is possible variously. First of all rectification and distillation of DMF or DMA should be conducted in the vacuum at a temperature not higher than 100° . Considerably is decreased yellowing, if we into the

spinning solution add the substances, which join amines for example bisulfate, bisulfite, oxalic either other nonvolatile acids, hexamethylenetetramine or other derivatives of formaldehyde, etc.

Page 86.

If fiber was obtained nevertheless yellowish, then they whiten it by acids or by oxidizers. During the utilization of acids occurs the hydrolysis of amidine grouping to the carbamide according to the diagram:



During the utilization of oxidizers amidine grouping is oxidized with the disappearance of double bond. Apparently, in this case occurs hydrolysis according to the diagram given above.

Virtually for obtaining pure-white fiber they treat it by solution of chlorite (5-10 g/l) at 90-95° in presence of hydrochloric acid (2-5 g/l) or by solution of sulfuric acid (5-10 g/l) at the same temperature. However, as a result of the prolonged bleaching of fiber in the acid medium and at a high temperature can occur the hydrolysis of cyano--groups and their transformation into the carbamide or carboxyl groups, as a result of which tensile strength of fiber deteriorates [5, 6].

Drawing of PAN-fibers in a plastic state.

PAN-fiber, just as all thermoplastic fibers, acquires its characteristic textile properties only after drawing in plastic state.

In process of extract of macromolecule of thermoplastic fibers they slip along fiber axis, being oriented lengthwise, and they are simultaneously stacked more evenly along the length and over section of fiber. In this case the deficiencies, which appeared as a result of too rapid a molding, are smoothed. Therefore the elastic properties of fiber are improved, is increased its tensile strength, strength with the loop or the knot, wear resistance are improved other physicommechanical properties.

To pull out freshly formed fiber is possible in hot water, in diluted hot solution of DMF or DMA in water, and also in dry form at higher temperatures (140-160°), i.e., in plasticization bath, in hot air or vapor.

As [7] was shown, for any fiber there is optimal degree of stretch, above by which its physicommechanical properties deteriorate. In this case, first of all, is decreased the strength of fiber with the loop or the knot, and also wear resistance. For the caproic fiber the optimal multiplicity of drawing at room temperature is 4.0, and at elevated 4.5-5.0.

Page 87.

For PAN-fiber, apparently, this optimal multiplicity of drawing during

the molding in water-DMF-baths is 7-8, during the drawing in organic baths 11-12, with the hot drawing of the fiber of dry spinning 12-15. It was also shown that the optimal value of the product of strength P for the elongation ϵ by water/aqueous molding is achieved after drawing of the freshly formed fiber at 100°, 6-8 times; during further drawing this value little is changed. For PAN-fiber of the good quality $P\epsilon=750-1000$.

Thus, process of molding is finished with drawing in water/aqueous bath at 100°; in process of secondary drawing at temperatures of higher than 100° to increase strength of fiber is possible only due to reduction in elongation [8].

Depending on temperature of water-DMF bath and content in it of DMF fiber succeeds in extending additionally (after small extract in process of spinning itself) 7-8 times; with higher temperatures (100°) and good quality of polymer it is possible to extend even 10 times. In this case, as has already been indicated, product $P\epsilon$ is changed little, but the strength of fiber to abrasion and number of double bends noticeably they increase/grow.

It was shown [9] that for PAN-fiber "temperature of transition of second kind" of polymer, i.e., temperature, below by which mobility of links along fiber axis is sharply retarded, is equal to 80-82° (for caprone temperature of second-order transition is equal to 65°, for nylon of 80°). Therefore the extract of fiber can be effective in the

medium of air or liquid, not containing DMF, only at a temperature higher than 80°.

During dry molding, after outlet/yield from spinning cell in fiber is contained 2.5-3% DMF; for successful drawing of PAN-fiber part of DMF from it is recommended to eliminate with washing. After this, the content of DMF is reduced to 1.75-2.0%. In the washed fiber DMF is distributed more evenly, as a result of which more uniform conditions for the drawing of the fiber are created. The time, necessary for thermo-drawing the fiber of dry molding, is determined by temperature. Thus, at 100° are required 5.0 s. [10]. Usually thermo-drawing fiber of dry molding proceeds at 140-160° for time from 1.0 to 2.0 s. [11].

Through exhaust pipe they pass hot air, mixed with water vapor, or nitrogen, heated up to 180°. Sometimes for the drawing thread or braid they pass over the surface of metallic "iron". In this case the fibers are warmed one-sidedly and extract it can be irregular. The thicker the braid of fibrils, the more irregularly their drawing will occur. It is necessary to also consider the humidity of the fiber, which enters the exhaust pipe or the iron. After washing in the water the fiber takes away with itself to 50% (from its weight).

Page 88.

Falling into the heated space, water vaporizes; because of this the temperature of fiber considerably is reduced in comparison with the

temperature of duct or iron, and drawing occurs not under given conditions. Therefore before the hot-drawing of PAN-fiber it should be blown out/blown off it or dried in the stream of heated air.

During drawing of dry fiber in duct or on iron for heating of fibers to ambient temperature is required for a while. As a result of the low heat transfer from the gases to the thread this time is 7-10 s.; thus, the way of thread in the duct or not the iron must be respectively extended, i.e., it is necessary to increase the time of extract. Thus, at the length of duct of approximately 4 m the rate of the passage of thread in the duct must not exceed 20 m/min.

Pull rate of PAN-fiber in plasticization baths, which contain water or other liquids, depends on rate of warm-up of fiber. In the liquid medium the heat transfer is great and after after 1 s. fiber acquires the temperature of bath. Therefore the drawing of the fiber in the plasticization baths usually is produced with the same rate, as molding. Thus, the rate of fiber upon the entrance into the plasticization bath can be equal to 5-10 m/min, and at the outlet/yield, after 6-8 multiple extracts, 30-80 m/min.

Imparting to PAN-fiber winding.

Staple fiber from polyacrylonitrile has oval shear/section and smooth surface, which adds slipperiness to this fiber. Therefore for obtaining from PAN-fiber yarn or for its treatment/processing in the

mixture with wool or in the mixture with the cotton/knock it is necessary that the fiber would possess adherence. For this purpose they twine it, adding to it the form, which reminds the form of wool fibers.

Crimped staple fiber nitron can be obtained in two ways: a) mechanically, subjecting fibrils to corrugation at elevated temperatures; b) creating natural crimp with spontaneous contraction of freshly spun fibers in baths, where occurs swelling of fibers or their plastification.

For creation of crimp is mechanically suitable only by twisted/bunched method of finishing nitronic fiber. After washing and extract in the plastic state the braid is dried by hot water (or they blow out/blow off by hot air), then they pass between two tightening rollers and they supply into the chamber, where the fiber undergoes compression. Chamber is warmed outside by hot water, by vapor or with the aid of the electricity. As a result of increasing the temperature of fiber the molecular bonds in the polymer weaken the separate links of macromolecules and can be shifted/sheared, i.e., fiber becomes plastic.

Page 89.

Passing to the plastic state through the chamber/camera and undergoing in it compression, each fibril is bent and acquires crimps of the required form. For an increase in strength of crimp of fiber they

maintain/withstand during the specific time at an assigned temperature. With this crimps are fixed/recorded, and fiber acquires the capacity to resist strains under the effect/action of the loads, tested by staple fibers during the textile treatment/processing. The strength of crimp of wool is equal to 100% with the loading of fibrils to 50% of the value of breaking load. The strength of crimp of the nitronic staple fiber, obtained mechanically, in the dependence on the temperature and the duration of corrugation composes 50% and it is above.

Optimum conditions of corrugation of nitronic fiber, obtained from DMF-solutions, are following: temperature of 140-160°; duration of processing/treatment - about 10 s. [12]. The temperature of corrugation can be considerably reduced, treating braid preliminarily in the bath with hot water (98-100°), which contains DMF. Crimp is obtained the same type, but its stability under the mechanical influences is reduced. Good results are obtained during the mechanical corrugation of nitronic braid in the steaming chamber/camera under the conditions for compression in the medium of water vapor with 0.7 atm(gage) [13].

As a result of corrugation tensile strength of fiber is reduced. The high temperature and the efforts/forces, created during the corrugation, worsen/impair the mechanical indices of fiber; extension at break and product P_l especially sharply is reduced.

Another method of creation of "natural" winding consists in processing/treatment of fiber in free state in bath, where occurs swelling of polymer or its plastification. This method of designing of winding has long ago been used in the production of the polyamide staple fiber, where processing/treatment of fiber is accomplished/realized in the baths, which contain a small quantity of sulfuric acid [14]. Natural crimp of the fiber appears as a result of weakening molecular bonds. The macromolecules, elongated along the length of fiber axis, attempt to be bent and they take in this case the more natural form. With the contraction of macromolecules along the length the significant contraction of fiber occurs.

Since spinning never occurs under strictly identical conditions (separate places of fibers they are formed more rapidly are tested larger tension, others they are formed more slowly and tension less), fibers are handled along the length dissimilarly, as a result of which appears required winding.

Page 90.

Natural winding is usually less uniform on form, but natural crimp is more stable than obtained mechanically, since it is fixed/recorded in state of equilibrium of fiber and therefore better it is retained under effect/action of mechanical loads. Furthermore, for the creation of natural crimp of the fiber nitron is not required to heat to the high temperature; it undergoes only processing/treatment in the water at 95-98° or in the brightening

solution during 30-60 s. Therefore during the creation of natural crimp the quality of fiber is not reduced. But on the other side, the creation of natural crimp is connected with the application of a more compound circuit of finishing.

In practice both methods of designing of crimp are used. Which of the methods is best, to solve is thus far difficult.

Brightening and preparation of nitronic fiber.

Problem of correct preparation is one of synthetic fibers most complex in production. However, the authors did not pose before themselves the problem of examining this problem in this book. One should only indicate that fiber nitron, just as the majorities of new hydrophobic synthetic fibers, absorbs a very insignificant quantity of water vapors from air (not more than 0.5% of its weight) and therefore it always remains "dry". Because of this appearing with friction and rewinding of nitronic fiber the electric charges do not depart from the surface of fiber, and during the textile treatment/processing it strongly is electrified. Voltage can reach 15000 V and more. The electrification of fiber impedes the processes of loosening, combing, spinning and drawing of the fiber, and also the processes of twist, weaving, binding, etc.

For preventing electrification of its nitronic fiber they subject to special treatment - they prepare. Preparation and imparting to

fiber winding are usually produced simultaneously - this is the latter/last wet operation before the drying of fiber. For the preparation about 40 g/l of the preparing composition use aqueous solutions or emulsions, which contain and heated to 60°. This operation can be produced during processing/treatment of nitronic silk on the latter/last decoration rollers, and also during processing/treatment of nitronic staple fiber in the braid (see Fig. 13, diagram a) or in cut form (see Fig. 13, diagram b).

As preparing substance it is proposed many mixtures of different composition. Those, which are added to the surface layer of fiber a certain hydrophilic behavior, are best. They include different hydroxyethylated compounds (OS-20, OP-10, Stearoks-6, etc.); and also the emulsions, which contain together with the preparations indicated triethanolamine or small quantities of ethylene glycol.

Page 91.

It is necessary that brightening preparation would satisfy following basic requirements.

1. In preparation must be included polyoxyethylated derivatives, which contain not less than 6-10 groups $\text{CH}_2\text{-CH}_2\text{-O}$.

Hydroxyethyl groups, being characterized by hydrophilic behavior, contribute to removal/distance of electrostatic charge from surface of fiber and they facilitate its textile processing/treatment thereby.

With the decrease of electrostatic charge is reduced the "sludge capacity" of nitronic fiber, which usually is sufficiently significant. So that the sludge capacity of nitronic articles after laundry would not increase/grow, hydroxyethylated preparations must be held down comparatively solidly by polyacrylonitrile. According to published data, for this purpose one should use the preparations, which contain in the molecule to 18-20 hydroxyethyl groups.

2) Brightening preparation must contain oils and emulsifiers, which raise the stability of emulsion, so that it would be possible to use the preparation composition at temperatures of bath of 90-95°.

3) Sometimes into the brightening composition it is necessary to introduce the leveler A or other adequate/approaching derivatives of quaternary ammonium bases/bases, which impart to nitronic fiber the capacity to be stained after the drying (see below).

Up to now still there is no sufficient quantity of data, that make it possible to make correct selection of preparation and to recommend specified conditions for brightening processing of nitronic silk or staple fiber.

Drying and thermal stabilization of nitronic fiber.

Drying and thermal stabilization of fiber is last operation in series of decoration operations. Nitron in the medium of air,

heated to 100-110°; the temperature of air it must not be higher than 120°, since in this case fiber can yellow. If for the preparation substances with a large number of double bonds (for example, the unpurified oleic acid) are used, then the temperature of drying must be lowered to 80-85°. Drying occurs rapidly, since nitronic fiber, in contrast to the viscose, does not hold down moisture. Usually in rack or chain dryers the drying of nitronic fiber lasts not more than 3 hours. In the finished fiber it is contained not more than 0.5% water.

Page 92.

Thermal stabilization of finished fiber nitron is produced after its drying, and sometimes simultaneously with it. Nitronic fiber, as all thermoplastic fibers, changes its of property with an increase in the temperature (so, the non-heat-fixed nitronic staple fiber it is handled in the boiling water to 15-17%), and therefore in the process of dyeing/coloring at 100° the significant contraction of nitronic articles occurs. At present for the liquidation of this deficiency nitronic staple fiber and nitronic silk subject to thermal stabilization. As a result of the thermal stabilization of nitronic fiber, especially in the medium of water vapor under the pressure, is increased the stability of crimp and the elasticity of fiber. Thus, the loop strength of nitronic fiber increases/grows from 50-55% to 80-85% and more.

Thermal stabilization of fiber is produced in free form or in the

form of tightly wound spools. Fiber is heated to the assigned temperature during the specific time. Process continues during three phases.

In first phase as a result of increasing in temperature and weakening of energy of molecular bonds mobility of links of macromolecules is raised and possibility of approach of separate dipole groups of adjacent molecules is increased.

In second phase new dipole bonds between dipoles of links, which are located in thermal agitation, are formed. This process occurs in the time and is accelerated, just as the processes of crystallization, 2.5-3 times with an increase in the temperature by each of 10° . Therefore the process of thermal stabilization to a considerable degree depends on its duration and temperature. At 160° in 10 s. is reached the same effect, that at 120° in 14 min. In the presence in the environment of vapors of solvent, for example DMF or water vapors, it is possible to reduce processing/treatment temperature on $15-20^{\circ}$, since molecules of DMF, and to a certain extent water vapors solvate the dipole groups of polymer and weaken/attenuate molecular bonds, i.e., they influence by such form as an increase in the temperature.

In third phase fiber is cooled. In this case the old and restrike dipole bonds are strengthened and summary energy of intermolecular interaction as a result of thermal stabilization increases/grows.

Degree of thermal stabilization is determined depending on further working of nitronic fiber or articles made of it, for example from dyeing/coloring temperature. It is empirically established that the effect of thermal stabilization remains stable at temperatures on 15-20° lower than temperature of fixation. Therefore if dyeing/coloring is produced at 100°, then thermal stabilization must be produced at a temperature not lower than 120°. Usually for the thermal stabilization of nitronic fiber is recommended the temperature not higher than 140° to avoid the yellowing of fiber and duration of this operation of approximately 10-30 s, in the dependence on the temperature and the presence in the apparatuses, where is performed this operation [15], of the water vapors or DMF.

Page 93.

Thermal stabilization is accomplished/realized in autoclaves, steaming chambers, ducts, warmed with the aid of electricity, or in any other similar apparatuses. It is necessary that in all apparatuses for thermal stabilization it would be possible to thoroughly regulate the temperature within limits of 0.5°, since the oscillations/vibrations of temperature have a strong effect on the effect of fixation [16].

Thermally stabilized nitronic fiber must be handled in boiling water for 0.5 hours not more than to 1%.

It was proposed for increasing in heat resistance and reduction in plasticity of nitronic fiber at elevated temperatures to treat spinning solution of PAN or fiber during finishing with vapors of formaldehyde or its derivatives (for example, by paraformaldehyde [17] or by its or derivatives [18]). As a result of chemical reaction are formed the cross methylene chemical bonds, which solidly cross-link macromolecules and thereby the raising heat resistance fibers. For the completion of chemical reaction the fiber after its processing/treatment must be heated up to 130°. However, for the fiber from polyacrylonitrile this processing/treatment is excessive, since the molecular bonds between the cyano-groups of PAN are so numerous and strong that fiber and without the processing/treatment by formaldehyde is sufficiently thermoresistant.

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Page 94.

Chapter 7.

DYEING.

General principles of dyeing/coloring nitronic fiber.

Dyeing/coloring of PAN-fibers is conjugated with significant difficulties, which complicate their application in textile industry. Difficulties during dyeing/coloring of PAN-fiber are explained: by the absence in the molecule of polyacrylonitrile of the functional groups, capable of joining the molecules of dye/pigment, with structure density of fiber and by the extremely low diffusion coefficient.

As is known, dyeing/coloring natural fibers (cotton, wool, natural silk) and synthetic fibers (on basis of cellulose) occurs as a result of formation of strong/durable chemical bonds between acid or basic groups of protein fibers (wool, silk) and basic or acid groups of dyes/pigments or as a result of formation of sufficiently strong/durable hydrogen bonds between groups OH of cellulose and carboxylic, hydroxyl or by amino groups of dyes/pigments. In both cases the dyes/pigments solidly are joined with the molecules of polymer. In the molecule of polyacrylonitrile there are no similar groups almost; therefore its durable staining/coloring in deep tones under the normal conditions is impossible.

In recent years high value acquired methods of dyeing/coloring synthetic fibers by dispersed (acetate) dyes/pigments, which do not have strong active groups. In this case the dyeing/coloring is explained by the dissolution of the molecules of dye/pigment in the polymeric substance. As numerous works showed, this process is determined by the rate of diffusion of the molecules of dye/pigment into the depth of fiber, i.e., by the diffusion equation of Fick [1]. The coefficient of diffusion of dyes/pigments in the aqueous solutions is equal, depending on the molecular dimension or assemblies of dye/pigment, 10^{-5} - 10^{-6} cm²/s. The coefficient of diffusion of the same dyes/pigments in the swollen gel is approximately 10^{-6} , in the viscose fibers and films 10^{-7} - 10^{-8} , in the cotton/knock of approximately 10^{-9} , in the caproic fiber of approximately 10^{-11} cm²/s. The coefficient of diffusion of dyes/pigments into the depth of PAN-fiber (for the dry fiber) does not exceed 10^{-12} - 10^{-14} cm²/s. Thus, under the identical conditions dyeing/coloring the caproic fiber is continued longer than viscose, 1000 times, and dyeing/coloring PAN-fiber 1,000,000 times.

Page 95.

The slow penetration of dye/pigment into the depth of PAN-fiber is explained by the fact that this fiber is incapable to swell in the aqueous solutions. The high density of the structure of PAN-fiber is explained by the rapid landing of polymer from the spinning solution into the medium, in which this polymer will not swell.

Diffusion coefficient, and consequently, rate of dyeing/coloring sharply is increased with increase in temperature. With an increase in the temperature on 10° diffusion coefficient and rate of dyeing/coloring increase/grow on the average 2.5-3.0 times. The identical depth of coloring is reached at 90° after 2.0 hours and at 140° through 30 cotter pins. Therefore the difficultly painted fibers, including PAN fiber, can be stained at temperatures on the order of $120-140^{\circ}$. But this the method of the high-temperature dyeing/coloring of PAN-fiber has a number of deficiencies.

With change in structure of fiber diffusion coefficient and rate of dyeing/coloring sharply are changed. Thus, during drawing of caproic fiber the diffusion coefficient and the rate of dyeing/coloring are reduced 1000 times [2]. The same effect/action exert thermo- and other processings/treatments, as a result of which the structure of fiber is thickened. Conversely, with the swelling of fiber or its contraction in the swollen state dyeing/coloring considerably is accelerated (100 or more times). Irregular coloring of articles made of the synthetic fibers is most frequently explained by the irregular density of the molecular structure of fibers. For the levelling of irregular dyeing/coloring frequently one should preliminarily steam synthetic fibers or conduct dyeing/coloring under the conditions for strong swelling, i.e., weaken/attenuate the structure of fiber.

Thus, for facilitating coloring of PAN-fiber there are two ways:

- 1) introduction to molecule of polyacrylonitrile of groups, capable of joining acid or basic dyes;
- 2) loosening structure of PAN-fiber in order to ensure more rapid penetration of dyes/pigments into depth of fiber.

Both methods supplement each other. During the introduction to the molecule of the polymer of active groups the dyeing/coloring is not accelerated, but coloring becomes more resistant to the laundries or to other or what processings/treatments. During loosening of structure the penetration of dye/pigment into the depth of fiber only is accelerated, but durable bonds are not formed and coloring without the additional measures proves to be unstable to the laundry and to other water/aqueous treatments.

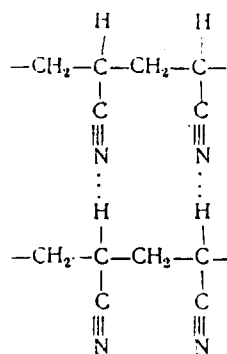
Polyacrylonitrile has only one type of polar of -group-cyano--group. They are electronegative and are capable of joining cations or groups of basic character. Bonds appearing in this case are very weak and disintegrate with water; but in certain cases even these weak bonds prove to be sufficient for the containment of the molecules of dye/pigment.

Page 96.

This relates first of all to large-size cations, for example to the cations of ammonium bases/bases, and also to the basic groups or the cations, capable of forming complex compounds with the cyano-groups.

To similar groups, as is known, relate amino groups, cations of copper Cu^+ , and apparently, the singly charged cations of ammonium bases/bases.

At the same time cyano--groups form comparatively strong/durable dipole and hydrogen bonds with methine groups of adjacent macromolecules, in consequence of which structure of polymer becomes to very strong/durable and it is difficult permeated for molecules of dye/pigment, which do not have affinity with cyano--groups. This structure can be depicted schematically:



In order to facilitate the penetration of dye/pigment into the depth of fiber, it is necessary to weaken/attenuate bonds $\text{N}\cdots\text{H}$, i.e., to solvate cyano--groups. For this purpose are suitable many compounds, easily generating hydrogen bonds, for example phenols, phenol-carboxylic acids, diphenyloxides, diamines of aromatic series, etc. Under the influence on the polymer of these substances are formed the molecular compounds of the type $-\text{C}\equiv\text{N}\cdots\text{HO}-\text{C}_6\text{H}_5$, and hydrogen bonds $\text{N}\cdots\text{H}$ between the macromolecules they weaken.

Besides large number of negative cyano--groups and neutral

methylene groups, in molecule of polyacrylonitrile through ends of chain, apparently, are located groups OH or COOH, and in the opinion of some researchers, also sulfate groups, if polymerization was produced in presence of persulfate. The presence of one or the other acid end groups depends on the form of catalyst, undertaken for the polymerization of acrylonitrile, but a quantity of them is small and is limited by medium molecular weight of polymers in the fiber. At the same time the presence of acid groups in the macromolecules of PAN contributes to the strong/durable (chemical) joining of basic dyes.

With molecular weight of PAN, equal to about 100.000, quantity of these terminal active groups composes $1 \cdot 10^{-5}$ equiv./g, i.e., it is approximately 5 times less than quantity of terminal amino- or carboxyl groups in caproic or nylon fiber.

Page 97.

According to experimental data, polyacrylonitrile or fibers, obtained from it, are capable of joining from $1 \cdot 10^{-5}$ to $5 \cdot 10^{-5}$ equivalent of alkali. Therefore PAN-fiber durably joins about $2.5-3.5 \cdot 10^{-5}$ equiv./g of basic dye [3]. The strength of coloring with its basic dyes must be the same as in the caproic fiber, painted by acid dyes, but a quantity of absorbed dye/pigment and depth of coloring must be 3-5 times more weakly.

Actually, it is known that a PAN-fiber is stained with basic dyes sufficiently solidly in the tones of average/mean intensity, but deep colorings to achieve is cannot.

It was proposed to introduce into the molecule PAN active carboxyl groups via the hydrolysis of cyano--groups by water or by carboxyl groups via the hydrolysis of cyano--groups by water or by acids, amidine groupings via processing a PAN-fiber by ammonia, amino group by processing a PAN-fiber by hydroxylamine.

During the introduction of carboxyl groups the joining of basic dyes is facilitated. The introduction of all remaining groups: carbamide, amino-, amidine - contributes to the strong/durable joining of acid dyes. This is especially important, since they usually process PAN-fiber in the mixture with wool, which is easily stained with acid dyes.

As has already been indicated, during introduction of different active groups dyeing/coloring is not accelerated, but strength of coloring only is raised. For accelerating the dyeing/coloring it is necessary to facilitate the access of dye/pigment into the depth of fiber. For this purpose into the dye bath are introduced the "carriers": phenols, phenol acids and other substances. In this case PAN-fiber will swell in the dye bath, and the rate of dyeing/coloring increases/grows many times.

It is possible to obtain loosened structure of PAN-fiber, forming it not from polymer, but from copolymer (see Chapter 8). It is known that with the damage of the structure regularity of polymer the intensity of molecular bonds is reduced, since the possibility of the formation of bonds $N \cdots H$ is decreased. As a result the structure becomes more accessible for the penetration of dye/pigment into the depth of fiber. A large number of copolymers of acrylonitrile with other different substances, capable of being formed into the fibers is at present known. However, the property of PAN-fiber - its high light resistance, a good heat resistance, good mechanical properties are retained only in such a case, when a quantity of links of

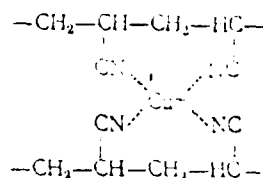
acrylonitrile in the copolymer is not less than 95-90%.

For obtaining looser structure of fiber it was proposed to also form fibers not of copolymers, but of mixture of two polymers.

Page 98.

Sometimes second monomer in copolymer or second polymer in mixture is simultaneously carrier of active groups COOH, NH₂, pyridine remainders/residues or other groups, capable of joining molecules of acid or basic dye. In this case in the presence of copolymer or mixture of polymers the absorption of dye/pigment not only is accelerated, but also is raised the strength of coloring.

One should mention even about series/number of methods, based on introduction to molecule of polymer or into molecule of very dye/pigment of such groups, which facilitate bond between dye/pigment and cyano--group. Among these methods first of all it is possible to name processing/treatment of PAN-fiber by salts of singly charged copper, for example by solution CuSO₄ in the reducing medium. The same group of methods includes processing/treatment of PAN-fiber by salts of ammonium bases/bases or by the brightening compositions, which contain such salts, and also dyeing/coloring PAN-fiber by the dyes/pigments, which contain in the molecule ammonium or other large/coarse cation groupings. In all mentioned methods, apparently, the discussion deals with the formation of complex compounds of the type [4]



Formed positively charged/loaded complex groupings are capable of joining acid dyes.

Is given below brief information about different methods of dyeing/coloring PAN-fiber, described in the literature, and also some consideration about worthwhileness of their application.

Dyeing/coloring the freshly formed PAN-fiber in wet form.

During dyeing/coloring of freshly formed PAN-fiber, obtained from solution in DMF using water/aqueous method, dye/pigment rapidly and in significant quantity penetrates depth of fiber [5]; this is explained by presence in freshly formed fiber of pores, filled with water. Dye/pigment diffuses into these pores from the dye bath at a velocity, which corresponds to its diffusion in the aqueous solution. In this case all classes of dyes/pigments penetrate the depth of fiber equally easily. The method of dyeing/coloring the PAN-fiber is suitable for acid, basic, straight/direct, dispersed and other dyes/pigments. In the dried out fiber the dye/pigment cannot penetrate in the depth of pores, and dyeing/coloring becomes impossible. With this method of dyeing/coloring the dye barely is connected with the molecules of polymer. Therefore with the washing of the painted fiber the

significant part of the loose dye/pigment is washed clean in water to the drying. But the drying of fiber after dyeing/coloring contributes to the affixing of dye/pigment in the fiber.

Page 99.

The higher the temperature of drying, the less the quantity of dye/pigment is washed out from the fiber with the subsequent washing or the soaping; after the drying of the painted fiber at 110-120° dye/pigment during the washing is not removed.

Operation of dyeing/coloring wet fibers can be produced by any at present method accepted; duration of dyeing/coloring can be abbreviated/reduced to 1 min. Dyeing/coloring temperature must be maintained within limits of 90-95°. Different mechanical loads and drawing of the fiber worsen/impair the evenness of its subsequent coloring.

Method of dyeing/coloring wet fiber, being at first glance simplest, meets series/number of difficulties in practice. First of all, for dyeing/coloring the fiber in the different tones special paint rooms are required. From the moment of spinning to its dyeing/coloring long time is passed sometimes. True, PAN-fiber can be stored in the wet form - in the rubberized bags, which do not pass moisture, 1-2 months, in this case its capacity to be stained does not disappear. However, with the transport of wet fiber in the rubber blankets the part of the water nevertheless can be vaporized, which

detrimentally is reflected in intensity and evenness of dyeing/coloring. However, at the textile factories not always it is possible to organize the drying of fiber, to process wet fiber into yarn or articles it is completely impossible.

Thus, this method of dyeing/coloring can find only limited application.

Dyeing/coloring PAN-fiber in a bath, which contains DMF, DMA or another solvent for PAN.

This method is modification of method described above. For accelerating the dyeing/coloring into the dye bath they introduce to 50% DMF [6]. In this case the fiber strongly will swell. Dyeing/coloring is produced for 1 hour at 30-60°. This method hardly will be able to find practical application, since as a result of the introduction to the dye bath of large quantities of DMF or DMA the process of dyeing/coloring considerably is raised in price and the harm of work in paint room is increased.

Dyeing/coloring with the additive to the dye bath of substances, which cause the swelling of polymer.

Large number of different substances, which facilitate dyeing/coloring PAN-fiber, was proposed. Among such substances practical value acquired, apparently, only to salicylic acids,

diphenyloxide and phenylene diamine. These "carriers" weaken/attenuate molecular bonds and thereby they cover the penetration of dye/pigment into the depth of fiber; after dyeing/coloring the fibers "carriers" are removed via washing.

Page 100.

For the effective effect/action of the additive it is necessary to dye bath in a quantity from 50 to 100 g/l, i.e., several times more than dye/pigment, as a result of which the process of dyeing/coloring strongly is raised in price. Furthermore, the majority derivative of phenol, which are toxic, are not washed clean completely from the fiber. Therefore the at present described method almost nowhere is used.

Dyeing/coloring PAN-fiber after its preliminary processing/treatment by salts of univalent copper.

This method of dyeing/coloring had extensive application, especially at first after appearance of PAN-fiber, when other methods of dyeing/coloring yet were not known.

As it was already indicated, univalent copper forms with cyano--groups complex compound, which has positive charge. Because of this charge PAN-fiber acquires the capacity to solidly join acid dyes

FOOTNOTE * The mechanism of joining by PAN-fiber of ions Cu^+ and molecules of dye/pigment is still insufficiently explained. Was assumed [7] that ions Cu^+ and dye/pigment are joined only by the acid groups of polymer [19]. ENDFOOTNOTE.

Before the dyeing/coloring PAN-fiber is treated by the solution of bivalent copper, for example by solution CuSO_4 , in the presence of reducer [8]; ions Cu^+ are sorbed with polymer, and complex groups are formed. Then in the same or in another bath is produced dyeing/coloring fiber with acid dyes under the normal conditions. Coloring is obtained by strong/durable to the laundry and it is sufficient deep. Deficiencies in this method are need of installation of two baths for the dyeing/coloring and the difficulty during the creation of reducing medium, since univalent copper in air easily is oxidized to the bivalent and coloring becomes irregular and lackluster.

Dyeing/coloring PAN-fiber by basic dyes.

As it was already indicated, basic dyes solidly stain PAN-fiber. At present more or is less established that the dyeing/coloring occurs on the end groups. A quantity of sorbed basic dye (from $2.0 \cdot 10^{-5}$ to $3.7 \cdot 10^{-5}$ equiv./g) is located in accordance with medium molecular weight of polymers; therefore dyeing/coloring can be considered as chemical binding of basis/base by the terminal acid groups (carboxyl or sulfate). Dyeing/coloring is produced under the normal conditions.

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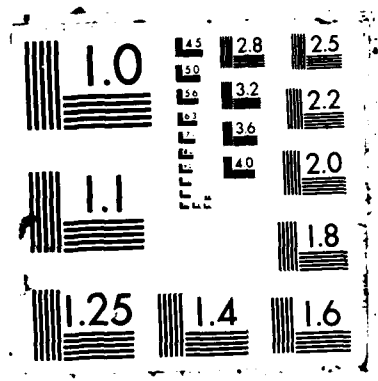
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in the presence of acid, but the duration of dyeing/coloring must be increased to 1-2 hours, and temperature is increased to 95°. Coloring is characterized by resistance to laundry [9], but the depth of coloring does not exceed average/mean tones.

Page 12,

This method of dyeing/coloring, apparently, is one of accessible and let us apply well in such cases, when dyeing/coloring in deep tones is not required.

Introduction to a fiber of ammonium or other cation-active compounds.

This method of dyeing/coloring is analogous to dyeing/coloring PAN-fiber, processed by salts of univalent copper. In both cases the complex compounds along the place of cyano--groups are formed or cation is joined by acid groups, after which becomes possible the joining of acid dye. But during processing/treatment of PAN-fiber by cation-active compounds or by salts of ammonium bases/bases simultaneously occurs the significant loosening of the structure of fiber and dyeing/coloring is accelerated. Therefore the method of dyeing/coloring PAN-fiber indicated can prove to be in the future most effective. To treat PAN-fiber by the compounds indicated is possible before its drying, for example, simultaneously with brightening processing/treatment [10]. In this case as the ammonium basis/base can be used the derivatives of triethanolamine, salt of ammonium bases/bases, polyvinylamine derivatives, etc. Processed thus fiber can be stained with acid dyes under the normal conditions; in this case coloring, stable to the laundry, is obtained. For processing the

fiber to the drying [11] were proposed to use a solution 1 g/l of melamine at 70°. It is possible to also introduce cation-active substances into dye bath [12]; these substances form with the acid dyes the complex compounds, which are capable of quantitatively being joined by fiber.

Application of special classes of dyes/pigments, which contain ammonium or other large/coarse cation-active groupings.

Recently appeared dyes/pigments of new class - basic dyes, in molecule of which are large ammonium or polymethine cations, so-called astragon or Sevron dyes/pigments [13]. They are used just as common basic dyes, i.e., in the acid dye bath, but they stain fiber into deep and stable to light/world and laundry of tone. The wide application of a new class of dyes/pigments will make it possible to overcome the difficulties, which appear at present during dyeing/coloring of PAN-fiber.

Dyeing/coloring PAN-fiber at elevated temperatures.

At 120-140° diffusion coefficient into fiber increases/grows into hundreds of times, in consequence of which becomes in practice possible dyeing/coloring of PAN-fiber by basic, acetate and other dyes/pigments in deep tones, resistant to streak.

However, the method indicated can be applied only in such cases, when at the dye factories is an installation for the high-temperature dyeing/coloring. Furthermore, in this case PAN-fiber must be subjected to thermal stabilization not at 120° as usually, but at 160°, which causes the yellowing of fiber and it is connected with the industrial difficulties.

Dyeing/coloring PAN-fiber in a mass.

It was proposed to stain not molded PAN-fiber, but PAN in mass, i.e., to introduce dye/pigment into spinning solution. In this case it is possible to obtain PAN-fiber, painted in deep and strong/durable tones only using the dry method of molding. For the beater coloring the suitable dyes/pigments of many classes, for example azo dyes, acid and basic dyes, leucoether/esters of vat dyes, disperse colorants, etc. [14]. This is explained by the fact that the majority of the classes of dyes/pigments easily is dissolved in DMF or in DMA. For the spinning solutions in the concentrated solutions of salts this method of dyeing/coloring is not applied, since in this case dye/pigment is not dissolved. With spinning from DMF-solutions into the water/aqueous or organic tank it is also not applied, since dye/pigment changes into the precipitation bath. In connection with this it was proposed to use for the beater coloring not the dyes/pigments, water-soluble or in DMF, but the pigments, not dissolved in the majority of solvents. In this case it is possible to stain in the mass the spinning solution and then to obtain bottom it

fiber by any method of molding. However, in the process of dyeing/coloring appear the same difficulties, which usually appear in the production during dyeing/coloring of other synthetic fibers in the mass by the suspensions of dyes/pigments.

Introduction to molecules of the polymer of carbamide or carboxyl groups.

As has already been indicated, with hydrolysis of molecules of PAN in acid medium carbamide groups usually are formed. In this case the possibility of the chemical binding of acid dyes in the acid medium with the carbamide group appears. Hydrolysis can be realized by treatment of finished fiber by acid at elevated temperatures, for example, in the process of bleaching. Furthermore, during molding of PAN-fiber from solutions $ZnCl_2$ and $CaCl_2$, is always observed the partial hydrolysis of cyano--groups to the carbamide; therefore the fibers, obtained from the salt solutions, apparently, always they can be painted by acid dyes. This method of processing PAN-fiber is of practical interest; however, with a deep hydrolysis the quality of fiber deteriorates.

Page 103.

In practice to regulate the depth of hydrolysis is difficult, as a result of which the dyeing/coloring is frequently irregular. For the creation of the identical conditions of hydrolysis it was proposed to treat PAN-fiber under the strictly assigned conditions by dilute acid

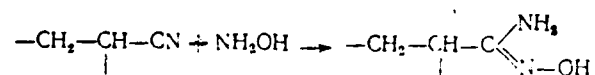
(pH=4.2-4.5) in the presence of hexametaphosphate ($\text{Na}_6\text{P}_6\text{O}_{18}$), or acid pyrophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, that play the role of buffer [15].

Treatment of PAN-fiber by the solutions of alkalis.

This method of dyeing/coloring fibers is variety of preceding method. It found use in GDR and in other countries because of its simplicity and cheapness. Finished PAN-fiber is treated in the course several days at 20° or during 1-2 hours at $50-100^\circ$ by the dilute solutions of alkalis (NaOH or of KOH). In this case the cyano--groups partially are saponified and are converted into the carbamide. The best conditions for processing/treatment proved to be the following: the concentration of solution KOH-4-8 g/l, the temperature of bath of $92-95^\circ$, the duration of processing/treatment 10-30 min [16]. Afterward to processing/treatment by alkali fiber becomes vivid-orange as a result of the formation of amidine groups, but during further processing/treatment by acid dyes in the presence of acids these amidine groups change into the colorless carbamide groups. The utilization of the too concentrated solutions of alkalis or excessively prolonged processing/treatment lead to sharp worsening/deterioration in the quality of fiber. Under standard conditions for processing/treatment the fiber loses not more than its 20% strength. Sometimes they recommend instead of the processing/treatment during 10-30 min. at $92-95^\circ$ to conduct processing/treatment during 2-3 min. by solution NaOH (30-50 g/l) at $120-130^\circ$ [17].

Introduction to a molecule of the polymer of amino group by processing PAN-fiber by the solutions of salts of hydroxylamine.

There is another method of dyeing/coloring, with which into molecule of polyacrylonitrile introduce amino groups by processing/treatment of PAN-fibers by solutions of sulfate or chloride of hydroxylamine. Reaction occurs according to the diagram



Processing/treatment lasts by 30 min. at 95° in the solution of sulfate of hydroxylamine, which has pH=6.5 [18]. After this processing/treatment the mechanical properties of fiber virtually are not changed.

Page 104.

Fibers acquires the capacity be stained to deeply with acid dyes, it is more weakly stained with direct dyes and ceases to be stained with basic dyes. The large toxicity of hydroxylamine is a deficiency in this method.

Methods of dyeing/coloring, connected with disturbance/breakdown of regular structure of polymer chains by copolymerization or by obtaining fiber from mixture of polymers, are indicated in following chapter.

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Page 105.

Chapter 8.

COPOLYMERS FIBER OF ACRYLONITRILE WITH THE VINYL MONOMERS OR FROM THE MIXTURES OF POLYMERS.

Polyacrylonitrile fibers can be obtained not only from pure/clean acrylonitrile, but also from copolymers of acrylonitrile with different compounds, or from mixtures PAN with other polymers. PAN, which possesses many valuable properties: by high light- and by heat resistance, by a good chemical stability, etc., has the number of essential deficiencies. Fiber from PAN with difficulty is stained and has yellowish hue. Pure/clean polymer PAN possesses regular structure and therefore it is dissolved in a small number of solvents and most frequently only during the heating.

In copolymers of acrylonitrile with other unsaturated compounds, most frequently with vinyl derivatives, molecular bonds considerably are weakened/attenuated due to damage of structure regularity. It is known that the copolymers of two initial monomers, the containing in the chain two types of links in an approximately equal quantity, considerably more easily are dissolved, than the polymers, which contain in the chain only the one form of links. In this case the melting point or beginning of softening copolymer is below, viscosity

of the solution with the identical content of substance in the solution is less and fiber is stained better.

Fibers, obtained of their copolymers of acrylonitrile or from mixtures PAN with other polymers, usually are formed from pure/clean PAN, they more easily than have brighter coloring and are characterized by increased softness and elasticity.

However, significant weakening of molecular bonds and decrease of structure regularity of copolymer is accompanied by worsening/deterioration in physicomechanical indices of fibers, obtained from copolymers. Chemical resistance also can deteriorate, if the second monomer contains ester groups; during the introduction to the molecule of the links of vinyl chloride the light resistance of fiber is reduced.

Page 106.

Initially the copolymers of acrylonitrile with other compounds were used in connection with this that these copolymers possess the best solubility in comparison with PAN; later they were adopted them for facilitating dyeing/coloring fiber.

Earlier extensively used copolymers of acrylonitrile with vinyl chloride or with vinyl acetate [1] (so-called Vinyon), that contain about 60% of acrylonitrile (fiber Vinyon N, Dynel, kanikalon, etc.). These copolymers easily are dissolved in the accessible solvents, for

example in acetone, and they can be molded both on the acetate fiber dry and using the wet process analogous. Many of these copolymers are softened during the heating and can be molded from the softened state. However, Vinyon, Dynel and other copolymers fiber of acrylonitrile, other 2-60% containing monomers, possess low chemical stability, and also high thermoplastic character and, consequently, low heat resistance. As a result of the significant damage of the structure of the polymer chain the major advantages PAN disappear. Therefore, in spite of the ease/lightness of dissolution and the simpler conditions of dyeing/coloring the fibers of the type of the Vinyon and other copolymer fibers from acrylonitrile, they are produced at present only on the small scales.

Fibers of type PAN in different countries are called only such, which consist of pure/clean PAN or of its copolymers, which contain not less than 85% acrylonitrile [2, 3]. In this case are retained all valuable properties PAN: resistance to heat and light, chemical stability, good mechanical properties of fiber, etc. Dyeing/coloring conditions simultaneously considerably are facilitated, since even with the small damage of structure regularity - in the presence in chain/network from 5 to 15% of other monomer units - diffusion coefficient is raised and the access of dye/pigment into the depth of fiber is facilitated.

Copolymers, which contain 85% and more than PAN, as a rule they are dissolved in DMF, DMA and other solvents for pure/clean PAN, and

fiber from these copolymers is formed with the same methods, as fiber from pure/clean PAN. At present because of the facilitation of dyeing/coloring conditions a quantity of fiber from such copolymers of that produced in many countries under different names, exceeds a quantity of fiber, formed from pure/clean PAN. As the second component with copolymerization are used vinyl acetate, vinylpyridine, acrylamide, acrylic esters, methylmethacrylate and other monomers, capable of copolymerizing with acrylonitrile. Are used also the triple monomeric mixtures, capable of being polymerized into the polymers of the assigned composition.

During introduction as second monomer of links of styrene [4] and other hydrocarbons of vinyl series/number plasticity of fibers and their to extensibility sharply is increased, but in this case are lost most valuable textile properties, inherent in fibers from PAN, in particular high elasticity.

Page 107.

During introduction to chain of copolymer of acrylonitrile of links of vinylpyridine, vinylamine, acrylamide [5] and other compounds, which contain basic groups. considerably is raised capacity of fiber to be stained with acid dyes, while during introduction to chain/network of acid groups, for example, during copolymerization of acrylonitrile with methacrylic or itaconic acid [6] capacity of fiber to be stained with basic dyes is raised.

In order to facilitate dyeing/coloring fiber from PAN, it was proposed to conduct copolymerization with several different monomers, but in all cases of property fibers were approximately identical, and with increase of number of different monomers in chain complexity of obtaining copolymer increases/grows. Therefore in practice most frequently use the copolymers, which contain not more than two monomers, moreover as the second component one of the named above [7] compounds most frequently is used.

It was proposed as second monomer to use vinyl chloride or other halogen derivatives in small quantities. Since during the introduction to the chain/network of chlorine atoms the light resistance of polymer is lowered, it is necessary after copolymerization to treat polymer by primary, secondary or tertiary amines [8]. In this case are obtained the copolymers, which contain in the chain/network instead of chlorine atoms of group with nitrogen atom. These groups add basic character to polymer, and fiber acquires the capacity to be stained with acid dyes.

Besides pure/clean PAN or its copolymers, which contain not less than 85% acrylonitrile, for production PAN-fibers repeatedly were proposed and extensively are used mixtures of two or even more than polymers, containing significant quantity PAN [9]. Among the fibers, obtained from the mixture of two polymers, Acrilan is most widely known. According to firm data the first component of mixture for molding of Acrilan, undertaken in a greater quantity, is the copolymer

95% acrylonitrile and 5% of vinyl acetate; the second - copolymer 50% acrylonitrile and 50% of vinylpyridine. Fiber Zefran also is obtained from mixture [10] of copolymer of acrylonitrile with methylacrylate, undertaken in large quantities, and a small quantity of polymer, which contains the groups, which are capable of joining the acid dyes (links of vinylpyrrolidone). Furthermore for the same targets were proposed to mixture PAN with cellulose acetate [11], with the withdrawals/departures of the natural silk [12, etc. 13].

While more rapid dyeing/coloring of copolymer fiber is explained by damage of structure regularity of polymer chain, for fiber from mixtures of polymers increase in rate of diffusion of dyes/pigments is explained by separation of mixture of two polymers during their molding of their joint spinning solution.

Page 108.

During the separation of mixture in the structure of fiber the pores appear, as a result of which is facilitated the penetration of dyes/pigments into the depth of fiber.

In contrast to copolymer fiber, which retains valuable properties only in such a case, when in macromolecule it is contained not less than 85% acrylonitrile, mixtures of two polymers can contain different quantities PAN, in this case fiber of them will possess valuable textile properties.

Thus, in the case of applying of copolymers or mixtures of polymers is facilitated dyeing/coloring PAN-fiber. Furthermore, are improved spinning conditions of fiber from the DMF or the salt solutions both on the dry and using the wet process and in a number of cases are improved the elastic properties of fiber.

At the same time appearance of new cation-active basic dyes (sevron [transliterated] and astragon) either introduction of different chemically active groups to molecule PAN by processing fiber by alkali, by hydroxylamine, by ammonia and the like facilitated dyeing/coloring PAN-fiber and to a certain degree decreased need of replacing pure/clean PAN by its copolymers or by mixtures with other polymers.

At present about 60% of all PAN-fibers are produced not of pure/clean PAN, but of copolymers or their mixtures.

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Page 109.

Chapter 9.

TEXTILE PROPERTIES OF A PAN-FIBER.

General information about the textile properties.

In spite of the fact that fibers from PAN or its copolymers appeared only recently, they conquered in textile industry general/common acknowledgement, and their application from year to year is expanded. From these new fibers are prepared the most different articles: wool or cotton type cloth, knitted wear, technical cloths, blankets, etc.

Especially extensively is used PAN-fiber instead of wool or in mixture with wool for preparing warm wool materials and in production of warm knit goods: jumpers, knitted articles, etc. The wide application of a PAN-fiber is explained by its specific and very valuable textile properties. Some of these properties are given in appendix III.

Fibers from PAN or its copolymers, which contain are more than 85% acrylonitrile, they are characterized by high light resistance, which exceeds light resistance of all textile fibers, with exception of glass.

Heat resistance of PAN-fiber is very high. According to different literature data, the fibers of PAN begin to disintegrate only at temperatures higher than 300° , while according to some data, even after heat treatment they retain to 50% more of their initial strength [1].

Is sufficiently high also chemical stability of PAN-fiber, especially during treatment by its acids, by oxidizers or by organic solvents. The resistance of fiber from PAN to alkalis is insufficient; during the processing/treatment by its weak alkalis or by ammonia it yellows, and during the processing/treatment by the concentrated alkalis, for example by a 40% solution of caustic soda, it disintegrates.

Persons advantage of fibers from PAN or its copolymers is low specific weight ($1.14-1.16 \text{ g/cm}^3$), and also high modulus of elasticity, thanks to which appearance of articles made of these fibers after warping is reduced.

Page 110.

Are given below some properties of a PAN-fiber Orlon; for the comparison are given the properties of polyamide fiber nylon [2]:

..eduction in the strength in the wet form, % ... 0 12.

Strength with knot, % ... 77 88.

Strength to break (in arbitrary units) ... 0.61 0.43.

Young's modulus (in arbitrary units) ... 59.0 48.2.

Relation of Young's modulus for wet and dry fiber ... 1.0 0.28.

Absorbtion of moisture, % ... 1.0 4.2.

Stability of sizes/dimensions ... good..average/mean.

Mechanical indices of PAN-fiber, and also its elastic properties can be changed over wide limits depending on spinning conditions and heat treatment [3]. The higher the degree of stretch of fiber, the greater the plasticizer content in the exhaust bath and the higher the temperature at the drawing, the higher tensile strength of fiber. Therefore from one and the same spinning solution it is possible to obtain fiber with tensile strength from 20 to 45 razr. km. Simultaneously is changed the brittleness of fiber, characterized by strength with the loop. So, of two forms of fiber of Wolkrylon [vol'krilon] [4] fiber of one form, obtained according to the rigid diagram of molding without the contraction, after drawing has higher tensile strength, but its strength with the loop does not exceed 25%, while fiber of another form - vol'krilon-2, utilized for the treatment/processing in the mixture with wool, has the lowered/reduced strength the increased elongation, but strength with the loop is increased to 45%.

During heat treatment of PAN fiber form of strain curve on diagram load - elongation considerably is changed. With an increase in processing/treatment temperature strain curve is raised more steeply, the modulus of elasticity is increased, extension at break is decreased, the fraction/portion of elastic deformations increases/grows [5]. For an improvement in the basic mechanical indices of fiber (elasticity, the fraction/portion of elastic deformations, strength with the loop) it is necessary that the temperature of heat treatment would be above temperature of second-order transition (for PAN of approximately $+80^{\circ}$) [6].

As it was already indicated, PAN-fiber is characterized by high heat resistance. It is raised still more during heating of fiber without the access of atmospheric oxygen. Table 6 shows a change in tensile strength of fiber Orlon during the prolonged heating.

PAN-fiber possesses sufficiently high cold-resistance, although at temperatures below minus of $20-30^{\circ}$ it becomes brittle and it is split lengthwise [7].

Page 111.

Brittleness of PAN-fiber and low resistance connected with it to abrasion are most serious deficiencies in fiber from PAN.

Abradability of PAN-fiber depends on form of microsection, i.e. on conditions of its molding. The more rapid coagulates polymer from

the spinning solution, i.e., is the harder the spinning conditions of fiber, the greater the internal vacuums (vacuole) in the microsection and the greater the tendency of fiber toward longitudinal decompositions [8]. According to experimental data [9], if strength to the friction of cotton fabric is accepted for 100%, strength to the friction of a similar cloth from the nylon exceeds 200%, from wool 120%, from Acrilan 60%.

Fibers from PAN possess following advantages. They are soft and do not irritate skin, struts to the bacteria and the microorganisms do not rot, little they are crumpled, but completely retain the folds and the accordion pleats, obtained by heat treatment. Fibers from PAN do not felt even in the mixture with wool. They are washed well in water and rapidly they dry; they retain well heat. Because of all enumerated properties a PAN-fiber is used for the manufacture of wool type articles. Therefore at present the large part of the fibers from PAN is produced in the form of wool type staple fiber. The continuous filaments (silk) from PAN are produced only in a small quantity for the technical needs.

Mixtures of 55-60% of PAN and 45-10% of wool and of 30-50% of PAN and 50-70% of rayon staple fiber commonly are used.

With obtaining of mixed yarn - from fibers PAN and wool - usually "are fitted" their physicomechanical indices, i.e. obtain fibers with tensile strength approximately 25 razr. km and extension at break

28-30%. Fibers are produced in the cut form with the length of 70-100 mm. For increasing the adherence with wool or during their utilization in the pure form, besides the corrugation, they sometimes add to fiber uneven surface, eating away fiber from the surface by reagents (for example, by the concentrated solutions of inorganic salts), i.e., causing the partial dissolution of polymer.

Table 6. Strength of fiber Orlon under the varied conditions for heating.

Условия нагревания	Прочность на разрыв разр. км		Газрывное удлинение %	
	сухого	мокрого	сухого	мокрого
Без нагревания (1) . . .	30,7	30,0	15,7	17,0
Нагревание 16 час. при 200° на воздухе (7)	17,9	13,9	9,3	9,1
То же в среде азота (8)	25,8	25,0	12,9	13,7

Key: (1). Heating conditions. (2). Breaking strength, разр, km. (3). Extension at break. (4). dry. (5). wet. (6). Without heating. (7). Heating 16 hours at 200° in air. (8). The same in nitrogen atmosphere.

Page 112.

Hydrophobicity of PAN-fiber and special feature of its treatment/processing.

In molecules PAN are absent chemical groups, capable of joining water. Therefore the hydrophilic behavior of polymer is equal to 0-0.5%. However, in the structure of a PAN-fiber are vacuums and fine/small cracks. As a result of the capillary effect is observed the attraction of water by the walls of vacuums and channels; therefore fibers absorb to 1.0-1.5% of moisture. The equilibrium absorption of water by a PAN-fiber depends on the spinning conditions and on the structure of fiber [10]. Absorbtion of moisture somewhat increases/grows during the replacement of pure/clean PAN to the copolymers (fiber Acrilan it absorbs more than 1.5%), and also after

dyeing/coloring of a PAN-fiber. Nevertheless for the common treatment/processing in the textile enterprises absorbtion of moisture by a PAN-fiber is insufficient.

As a result of hydrophobicity of polymer electric charges, which appear with rewinding of threads or with carding and spinning, do not manage "to flow" from fiber and are accumulated, creating stress/voltage, which reaches several thousand volts. In this case the textile treatment/processing of a PAN-fiber under the normal conditions becomes impossible. The generally accepted measures - improvement in the humidity in the textile shops to 70%, the ionization of air, etc. - are not in this case effective. Only after processing/treatment of fiber from PAN and its copolymers by the special preparing substances (see above) it is possible to process them without the difficulties.

Therefore chemical plants must produce PAN-fiber, processed appropriate by compositions. Finished fiber must contain to 2% of preparation from its weight. As has already been indicated, the preparing composition must contain the substances, which impart to fiber softness and facilitating the removal/distance of electric charges. Sometimes for strengthening the antistatic effect/action in the composition of the preparing substances introduce glycol, glycerin or other hygroscopic compounds or the special static eliminators, which contain the derivatives of phosphoric acid.

By low hygroscopicity of PAN-fiber is explained also retarding/deceleration of diffusion of moisture and low moisture permeability of articles made of it. As a result of low moisture permeability the conditions for the utilization of articles made of PAN as the outer clothing, linen and knitted wear deteriorate. At the same time low moisture permeability and high capacity to create electric charges are favorable for the preparation/manufacture from a PAN-fiber of the so-called medical linen.

In the case of applying PAN-fiber in mixture with wool or in by rayon staple fiber considerably increases/grows moisture absorbtion of yarn and are improved hygienic conditions for utilization of articles.

Page 113.

If yarn from pure/clean Vol'krylon usually absorbs 1.3% of moisture, then during the preparation/manufacture of yarn from the mixture of Vol'krylon with the rayon staple fiber (50:50, moisture absorbtion increases/grows to 6.5%. In accordance with the requirements of hygiene by the lowest permissible limit of the moisture absorbtion of textiles it is usually considered 4.5%. The structure of the weaves of cloth or the method of the binding of knit goods has also high value for moisture permeability.

At present difficulties due to lowered/reduced moisture permeability of articles made of PAN-fiber are completely overcome, and this fiber can be used in any assortment of articles.

Thermoplastic character of a PAN-fiber and new possibilities of changing its textile properties.

Fiber from PAN, just as of many polymers of polyvinyl, polyamide and polyester series/number, possesses increased thermoplastic character. True, in contrast to the majority of fibers a PAN-fiber is characterized by high heat resistance, but during the heating in dry air to 140-150° or in the humid air up to 130° it acquires to plasticity and to take the assigned form. Its this property can be used for the imparting to fiber or to the article made of it of new textile properties.

Above it was indicated, that by thermo-drawing or thermal stabilization of PAN-fiber at plant of synthetic fiber it is possible within significant limits to change tensile strength, elongation, capacity to resist contraction in boiling water, etc. However, simultaneously with the fixation during the heat treatment of fiber considerably is thickened its structure, in consequence of which the dyeing/coloring is retarded. All hot workings, by which undergoes a PAN-fiber or articles made of it, must be conducted at a very accurate (in limits of 0.5°) temperature to avoid the appearance of striation and other defects of coloring.

Besides thermal stabilization and thermo-drawing, that are necessary operations at plants of synthetic fiber, in production of

PAN-fiber for creation on cloth or on knitted wear of new effects it is possible to use thermoplastic character of this fiber. Since this operation to more conveniently conduct on the finished article, the cloth or the knit goods after dyeing/coloring, then additional heat treatment usually is produced not to textile factory. This heat treatment makes it possible to create on the cloths from a PAN-fiber the constant, not disappearing folds, accordion pleats and designs. For this of cloth or article they subject to compression or pressing at 120° in the steaming chambers/cameras or at 140-160° in the air medium during the specific time, after which of they quench to the temperature lower than 70°.

Page 114.

Because of the fixation of the strains, created at high temperatures, the folds and accordion pleats do not disappear during the utilization of cloths or articles even during their prolonged storage in the water.

Another form of utilization of thermoplastic properties of PAN-fiber is obtaining so-called "volumetric" yarn. This yarn differs from the common the fact that a significant quantity of air contains and therefore it possesses high thermo-insulating properties. Articles made of such a yarn, are characterized by softness, they are fuzzy and little they are heat conducting, i.e., "they hold down well" heat. It is most expedient to prepare outer clothing from this cloth.

For creation of volumetric yarn PAN-fiber of two forms is mixed: one of them preliminarily is subjected at plant of synthetic fiber or at textile factory (in the form of thread) to drawing with thermal stabilization, but fiber another form (thread or fiber) is not subjected to similar processing/treatment and therefore it can be handled in hot water or during heating. Usually at the chemical plant during the molding they pull out the part of a PAN-fiber in the braid and they fix/record in this position, treating at a high temperature; another part of the same fiber they pull out without hot working [11]. After cutting and finishing both types of fiber are packed separately and they direct to the textile factories, where them are mixed into yarn in relationship/ratio 1:1. Instead of two forms of fiber it is possible to prepare thus two forms of yarn. It is possible to also treat fibers of both views of chemical plant in the cut form. In this case the fiber of one form after cutting is treated by hot water, as a result of which it considerably is handled; fiber of the second form is washed in cold water, and it is not handled.

With mixing and to processing/treatment by boiling water of fibers or yarn of two forms, of which one is capable of being handled in hot water, and another it is fixed, volumetric yarn is obtained. In this case the fiber, which was not undergoing contraction or fixation in the hot water, is handled to 17-20%, but the thermally stabilized or seated fiber - on is more than to 1%. As a result of different contraction of fiber yarn becomes fuzzy and volumetric.

Apparently, possibilities of utilization of thermoplastic character of PAN-fiber for imparting to it new textile properties are as yet far from exhausted, and in future it is possible to expect appearance of yarn or articles with new effective properties.

At present, besides heat treatment of synthetic fiber at plant, articles made of PAN-fiber are subjected to secondary thermal stabilization at textile factory. This is explained by the fact that during the strong thermal stabilization of fibers from PAN, as a result of which it is fixed/recorded from form and are added by them nonshrinking properties, dyeing/coloring articles considerably is retarded.

Page 115.

Therefore fibers from PAN are subjected to the initially preliminary heat treatment, sufficient so that the articles during the dyeing/coloring would not lose their form. Since dyeing/coloring usually is produced at 95-98°, and for retaining/maintaining the sizes/dimensions of fibers preliminary fixation at a temperature on 15-20° higher than temperature of their subsequent processing/treatment is necessary, then at the chemical plant heat treatment in the steaming chambers/cameras or the drying apparatuses at 110-115° is conducted.

After dyeing/coloring finished article is thermo-fixed/thermo-recorded additionally so that it during

utilization would not change form and it was not handled. One should use the following conditions of thermal stabilization at the textile factories of finished articles made of the pure/clean PAN-fiber without the admixture/impurity of wool:

a) processing/treatment by hot dry air at 180-195° during 20-30 s. (during the application of copolymers fiber temperature it can be lowered on 10-15°);

b) processing/treatment by hot humid air at 125-130° during 30 min. (in this case during processing/treatment of copolymers fiber PAN the duration of heat treatment can be reduced);

c) processing/treatment by the hot solution of formic acid (3 g/l) on drying-stretching frames, but this thermal stabilization it is not completely sufficient; after processing/treatment in the boiling water of articles they are capable of being handled to 6%.

For mixed yarn from PAN-fiber and wool fixation is necessary only in such a case, when content of PAN-fiber in mixture exceeds 50%. In the presence of wool of article it is better to subject to wet treatment or processing/treatment by humid air, since wool does not maintain/withstand high temperatures.

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Page 116.

Chapter 10.

REGENERATION OF CHEMICALS.

Prime cost of fibers of PAN and its copolymers considerably lower than prime cost of other synthetic fibers, for example polyamide and polyester/polyether. This is explained by the low cost/value of initial polymer, by the insignificant flow rate of basic chemicals, vapor and water in the process of obtaining the fiber and by the small energy content of production. Are given below expense norms in obtaining 1 kg. of staple fiber from PAN (according to tentative foreign data):

Source material, kg. ... 1.05.

Solvent (taking into account regeneration), kg.

DMF or DMA ... 0.12.

glycerin ... 0.03.

EK ... 0.10.

Brightening preparations, kg. ... 0.06.

Vapor (depending on method of regeneration) kg. ... to 50-70.

Electric energy, kWh ... 2.2.

Water, m³ ... 0.2.

Small quantity of withdrawals/departures of spinning solution, filter presses during cleaning, and also small quantity of servicing waste-spinner can be newly used in the form of polymer for production of fiber, if initial polymer it is sufficient pure and spinning solution is filtered well.

Low consumption of solvent, used for dissolution of polymer, can be achieved/reached only in its complete regeneration from steam-air mixture or from precipitation bath. The method of regeneration depends on the character of the solvent used.

On majority of plants, which produce PAN-fiber, as solvent DMF or DMA is used. For the dissolution 1 kg. of polymer it is required from 4.0 to 6.0 kg. DMF or DMA. Since these substances of road and their discharge/break into the waste water as a result of the toxicity it is hindered/hampered, necessary complete solvent recovery.

Boiling point DMF is equal to 154°, pressure of its vapor at different temperature is characterized by curve, depicted on Fig. 1.

Page 117.

From given data it is evident that at 20° in 1 m³ of air a very small quantity of vapor DMF is contained. By basic difficulty with the rectification of the mixtures of DMF with the water or during removal

DMF of water via its distillation is the thermal breakdown of this solvent at a high temperature [1].

In technical DMF small quantity of formic acid and dimethylamine or their salt is always present.

When, in DMF, acid and basic compounds are present, hydrolysis DMF with formation of formic acid and dimethylamine is accelerated. At 150° hydrolysis is very perceived. Thus, as a result of the losses by DMF with the rectification and distillation of solvent its expenditure/consumption considerably is increased. Therefore rectification and distillation DMF should be accomplished/realized at a temperature not higher than 100°, i.e., in the vacuum (650 mm Hg).

DMF forms with water sufficiently strong/durable hydrates, which consist of 1 molecule DMF and 3-4 molecules of water. But these hydrates of strut only at a temperature lower than 60°; with the rectification or the distillation they are decomposed. Furthermore, DMF somewhat destroys steel and other materials, which contain iron. In connection with this the process must be conducted in the equipment made of special steel, with a reduced temperature and at the reduced pressure (not above 100 mm Hg).

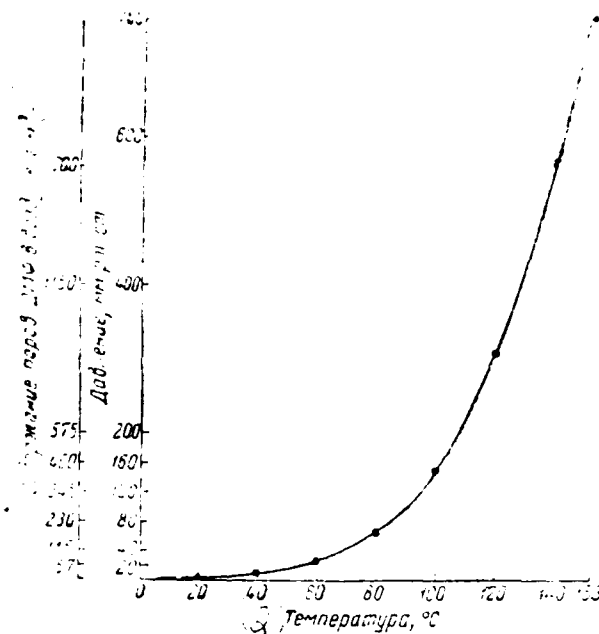


Fig. 16. Content in air and pressure of vapor DMF at different temperature.

Key: (1). Content ripping of DMF in air, g/m³. (2). Temperature, °C.

Page 118.

Method of regeneration DMF depends on method of spinning.

During molding of staple fiber in a water/aqueous manner from DMF-spinning solutions, which contain 15.5% PAN, and during coagulation of spinning solution in 60% solution DMF in water into precipitation bath enter about 6.5 kg. of spinning solution, and consequently, 5.5 kg. DMF. From this quantity in the precipitation bath remain about 2.75 kg. DMF, in the exhaust baths of approximately 2.7 kg. and in the bath of relaxation of approximately 0.05 kg.

After output/yield from bath of relaxation in fiber still are contained about 0.05 kg. DMF (on 1 kg. of fiber), which must be distant in wash baths.

Thus, during correct organization of countercurrent washing into sewerage must be dehydrated, which contains only tracks of DMF, but its loss in production theoretically must not exceed 0.05 kg/kg.

In baths of relaxation are accumulated about 0.3% DMF, in exhaust baths its concentration reaches 15-16%. In the precipitation bath the water is accumulated by DMF and diminishes; its quantity is completed by addition to this bath of the corresponding quantity of exhaust bath. To regeneration only exhaust bath is directed.

To regenerate DMF, which is contained in exhaust bath, is possible by two methods: extraction DMF by solvent, which does not mix with water, or by rectification of water/aqueous mixture DMF.

For extraction, until now, methylene chloride, dichloroethane and other chlorine-bearing hydrocarbons [2] were used, but investigations showed that distribution coefficient DMF between water and chlorine-bearing hydrocarbon was small. Therefore significant part the DMF is not extracted from the water, which is explained by high hydrophilic behavior DMF. Because of this the method of the extraction DMF from the water/aqueous mixtures it is in practice

unsuitable and at present it is not used.

It is profitable whether to economically use method of rectification of mixtures of DMF with water, they determine only, judging by concentration DMF in water/aqueous mixture. In the rectification column on 1 kg. DMF (if its content in mixture 15%) it is necessary to distill about 6.5 kg. of water or, taking into account the reflux ratio of rectification column, the equal to 1.3, about 9.0 kg. of water. For this purpose it is necessary to expend approximately 10 kg. steam. In this case on 1 kg. of fiber [3] is spent 65 kg of steam.

Thus, steam consumption is very great. With the higher concentration DMF in spinning solution (20%) and in bath, steam consumption is reduced to 40 kg. per 1 kg. of fiber).

With dry method of fiber formation by spinning usually in concentrated spinning solution containing up to 30% PAN, and for 1 kg. of fiber about 2.8-3.0 kg. DMF are expended/consumed.

Page 119.

The large part of the solvent in the spinning cell vaporizes into air and enters the recuperation in the form of air-steam mixture (PVS). DMF it is possible to absorb from PVS by water, by activated carbon, and also to condense by cooling PVS to 0° or to -5°.

Since pressure of vapor DMF is small, and its concentration in PVS, which emerges from spinning cell, reaches usually 25 g/m³ and it is above, it is most profitable to allot DMF from mixture by freezing. It was calculated, that in this way it is possible to regenerate 98% . . . in this case its theoretical flow rate per 1 kg. of fiber is reduced to 0.05 kg.

In the case of spinning of fiber in organic baths the same spinning solution is used, that with water/aqueous method, and into organic bath enters large part DMF from spinning solution. Most frequently as the precipitation bath glycerin or glycols, which contain about 20% DMF, are used. After spinning, they direct into the organic exhaust and wash bath, in which still is contained certain quantity DMF, also, to 1.5 kg. of organic precipitant on 1 kg. of polymer. Since in the precipitation bath usually is contained not more than 20% DMF, its regeneration, just as with the water/aqueous method of molding,

is reduced to the rectification of the mixture of organic precipitant and DMF. This mixture contains very little water, which is distilled easily and with the low expenditure of vapor; for the distillation/removal DMF also it is not required high steam consumption

Expenditure of glycerin or glycol for 1 : of fiber is very small, since these precipitators are taken away by fiber insignificantly and with countercurrent washing are accumulated in

wash waters: they are easily regenerated via rectification of water/aqueous mixtures.

In the case of applying of other precipitants, for example hydrocarbons, fatty acids, etc., apparently, seriously hinders regeneration DMF, but information about its regeneration from these precipitation baths are not thus far published.

DMA I regenerate by the same methods, then DMF. In both cases it is necessary to consider the light hydrolysis of amides in the aqueous medium at elevated temperatures. Besides the fact that in this case the losses of solvent are increased, occurs also the yellowing of spinning solution and fiber, since as a result of the hydrolysis amines are formed. Therefore frequently for retarding of hydrolysis, decrease of losses and averting of the yellowing of fiber with the rectification or the distillation DMF or DMA into the distillers add oxalic or other nonvolatile acids, which do not cause the excessive corrosion of equipment, or acid salts (bisulfates, bisulfites, etc.), derivatives of formaldehyde, etc. During the addition of these substances the expenditure/consumption DMF or DMA with the distillation or the rectification is reduced and the quality of the purified solvent is improved.

Page 120.

Otherwise produce the regeneration used as the solvent PAN of the concentrated aqueous solutions $ZnCl_2$, and other inorganic salts, and

also EK. In this case the regeneration is reduced to a vacuum-distillation/removal of water from the precipitation bath for the purpose of its transformation into the solvent for PAN. Flow rate EK, $ZnCl_2$, and other substances depends only on the correct organization of countercurrent flow and mixing of wash and exhaust baths, while steam consumption depends on the concentration of these compounds in the water. The excess of water must they will be distilled in the vacuum evaporating apparatuses.

Flow rate EK or $ZnCl_2$, is determined only by losses with sputtering, since in washed fiber virtually it is not contained these compounds; flow rate EK or $ZnCl_2$, theoretically must not exceed 0.01-0.03 kg. on 1 kg. volokna¹.

FOOTNOTE ¹. According to published data EK in the aqueous solutions at temperatures of ~80-100° it undergoes hydrolysis, being decomposed into ethylene glycol and CO_2 . Hydrolysis EK can lead to a significant increase in its flow rate. ENDFOOTNOTE.

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Page 121.

Appendix 1.

THE RATE OF COPOLYMERIZATION.

Many organic matter, incapable to be polymerized, enter into reaction of copolymerization with other unsaturated compounds. Thus, the derivatives of maleic and fumaric acids, glycol, diamines, etc. in the pure form are not polymerized, but they copolymerize, for example, with acrylonitrile.

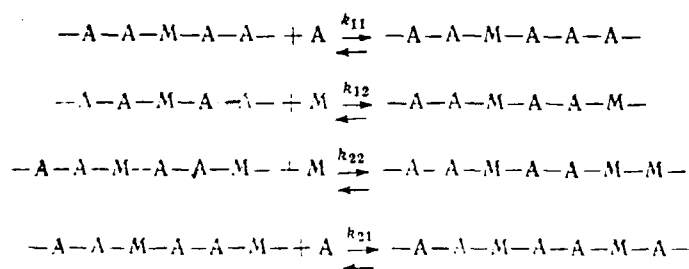
Because of application of method of copolymerization it becomes possible to considerably increase number of polymers of substances initial for obtaining, and consequently, to synthesize polymers with different properties.

Distinctive special feature of process of copolymerization is more complex mechanism of chain growth and fundamentally different kinetics of process itself in comparison with kinetics of separate polymerization of the same components. Apparently, the behavior of any macroradical caused only by its end link with the free valence and does not depend on nature of remaining links [1, 2].

However, for obtaining copolymer of desired composition must be determined, which must be quantitative composition of the starting material of monomers, since different monomers enter into reaction of

copolymerization with different rate. For example, methylacrylate reacts more rapidly than acrylonitrile. Because of this the relation of the content of the links of methylacrylate of the contents of monomers in the still unreacting initial mixture. Knowing relative reactivity of each component of reaction, it is possible to determine the necessary (for obtaining this polymer) composition of the starting material by mathematical calculation.

Let us examine reaction of copolymerization of acrylonitrile A and methylacrylate M. Let on the end of the growing one copolymer chain be located the link of acrylonitrile and at the end of another of methylacrylate M. Then in the reacting system can flow/occur the following concurrent reactions:



Page 122.

In these equations symbol k_i designates rate constant of corresponding reaction

k_{11} - reaction rate constant between copolymer chain, when on its end is located A, and monomer A.

k_{12} - reaction rate constant between copolymer chain, when on its

end is located A, and monomer M.

k_{22} - reaction rate constant between copolymer chain, when on its end is located M, and monomer M.

k_{11} - reaction rate constant between copolymer chain, when on its end is located M, and monomer A.

Obviously, relative reactivity of monomers can be expressed through relation of corresponding reaction rate constants. Thus, relative reactivity of acrylonitrile

$$r_1 = \frac{k_{11}}{k_{12}}$$

and methylacrylate

$$r_2 = \frac{k_{22}}{k_{21}}$$

Values r_1 and r_2 are more in substances, which possess greater tendency toward autopolymerization.

According to literature data [3], constants of copolymerization are constant values. Values r_1 and r_2 are not changed in the presence of different additives, for example water, benzene, ethylacetate, ethylbenzene, etc., and they do not depend on a quantity of catalyst and, consequently, from the general/common reaction rate. They are not changed, apparently, and during the copolymerization in it testifies about a change in the mechanism of process.

Knowing r_1 and r_2 , it is easy to calculate approximate

composition of the starting material of monomers for obtaining copolymer of specific composition.

Example. It is necessary to obtain the copolymer, which contains 75% of weight of acrylonitrile and 25% of weight of methylacrylate. For calculation let us apply the integral form of the kinetic equation of the copolymerization

$$C = \frac{(P-1) + \sqrt{(1-P)^2 + 4Pr_1r_2}}{2r_1}$$

Here C - molar relationship/ratio of monomers in the initial mixture;

P - molar relationship/ratio of the links of monomers in the polymer.

In our example

$$P = \frac{75}{53} : \frac{25}{86} \equiv 4,84$$

From table of relative reaction rates (see below) we find $r_1=0.67$; $r_2=1.26$. Hence to 1 mole of methacrylate it is C of the moles of acrylonitrile:

$$C = \frac{(4,84 - 1) + \sqrt{(1 - 4,84)^2 + 4 \cdot 4,84 \cdot 0,67 \cdot 1,26}}{2 \cdot 0,67} = 7,0$$

Consequently in initial mixture must be contained by 81% of weight of acrylonitrile and 19% of weight of methacrylate.

Relative reactivity of different monomers with acrylonitrile at 60°.

(1) Мономер	1	2
Акриламид ² (2)	0,875	1,357
Аллилхлорид ³ (3)	3,0±0,2	0,05±0,01
1-Ацетокен-1,3-бутадиен ⁴ (4)	0	0,7
α-Ацетоксистерол ⁵ (5)	0,08±0,01	0,4±0,05
1,1-Бис-(п-анизил)-этилен ⁶ (6)	0,014±0,002	0
1,1-Бис-(п-хлорфенол)-этилен ⁷ (7)	0,024±0,003	0
Бутадиен ⁸ (8)	0,0±0,04	0,35±0,08
Бутилакрилат ¹⁰ (9)	1,003±0,012	0,005±0,005
Винилацетат ¹¹ (10)	4,05±0,3	0,051±0,013
То же ¹² (11)	6,0	0,07
Винилбензоат ¹³ (12)	5,0±0,05	0,05±0,005
Винилиденхлорид ^{13,14} (13)	0,91±0,1	0,37±0,1
Винилформат ¹⁴ (14)	3,03±0,05	0,04±0,005
Винилхлорид ^{15,16} (15)	3,28±0,06	0,02±0,02
Винил-2-этилгексоат ¹⁶ (16)	12±2	0,01±0,01
Винилэтиловый эфир ¹⁷ (17)	5,0	0
Гексен-1 ¹⁸ (18)	12,2±2,4	0
Гексин-1 ¹⁸ (19)	5,4±0,5	0
Дифенилацетилен ¹⁹ (20)	13,6±1,0	0
1,1-Дифенилэтилен ²⁰ (21)	0,028±0,003	0
2,5-Дихлорстирол ²¹ (22)	0,19	0,07
Диэтилмалеинат ²² (23)	12,0	0
Диэтилфумарат ²³ (24)	8,0	0
Изобутилен ²⁴ (25)	1,02	0
Изопре ²⁵ (26)	0,03±0,003	0,45±0,05
Кроотоновая кислота ²⁶ (27)	21±10	0
Малеиновый ангидрид ²⁷ (28)	6	0
Метакролеин ²⁸ (29)	0,03	2,0
Метилакрилат ²⁹ (30)	0,67±0,1	1,26±0,1
Метилакрилонитрил ³⁰ (31)	0,32	2,68
Метилвинилкетон ³¹ (32)	0,61±0,04	1,78±0,22
Метилметакрилат ³² (33)	0,15±0,07	1,2±0,1
Метилстирол ³³ (34)	0,03±0,02	0,1±0,02
То же ³⁴ (35)	—	0,55±0,005
o-Метилстирол ³⁵ (36)	0,03±0,05	0,33±0,1
Метил-α-хлоракрилат ³⁶ (37)	0,15	2,0
Метилпиперидат ³⁷ (38)	0,15±0,07	1,2±0,14
Стирол ³⁸ (39)	0,01±0,04	0,41±0,08
Тетрахлорэтилен ³⁹ (40)	470	0
3,3,3-Трихлорпропен ⁴⁰ (41)	12,2±1,2	0,10±0,015
Трихлорэтилен ⁴¹ (42)	67	0
Хлорпропен ⁴² (43)	0,01±0,01	6,07±0,57

Key: (1). Monomer. (2). Acrylamide. (3). Allyl chloride. (4). 1-acetoxy-1,3-butadiene. (5). α -Acetoxystyrene. (6). 1,1-Bis-(n-anisyl) -ethylene. (7). 1,1-Bis-(n-chlorophenol) -ethylene. (8). Butadiene. (9). Butylacrylate. (10). Vinylacetate. (11). The same. (12). Vinylbenzoate. (13). Vinylidene chloride. (14). Vinylformate. (15). Vinyl chloride. (16). Vinyl-2-ethylhexoate. (17). Vinyl ethyl ether. (18). Hexene-1. (19). Hexyne-1. (20). Diphenylacetylene. (21). 1,1-Diphenylethylene. (22). 2,5-Dichlorostyrene. (23). Diethylmaleate. (24). Diethylfumarate. (25). Isobutylene. (26). Isoprene. (27). Crotonic acid. (28). Maleic anhydride. (29). Metacrolein. (30). Methylacrylate. (31). Methylacrylonitrile. (32). Methyl vinyl ketone. (33). Methylmethacrylate. (34). Methyl styrene. (35). The same. (36). o-Methyl styrene. (37). Methyl- α -chloroacrylate. (38). Methyl cyanamate. (39). Styrene. (40). Tetrachloroethylene. (41). 3,3,3-Trichloropropene. (42). Trichloroethylene. (43). Chloroprene.

Page 124.

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Appendix II.

THE SOLVENCY OF SOME ORGANIC COMPOUNDS WITH RESPECT TO
POLYACRYLONITRILE.

Material given in table characterizes capacity of different organic compounds to dissolve polyacrylonitrile. The parameter of solubility δ_p was calculated according to the data available in the literature about the heat of vaporization at 25° according to the formula

$$\delta_p = \left(\frac{L_v - RT}{V} \right)^{1/2}$$

where L_v - heat of vaporization, cal/mole;

T - absolute temperature, °K.

V - molal volume, equal to M/d (here M - molecular weight of substance, and d - its density).

In such cases, when corresponding data in the literature there was not, values L_v were calculated from boiling point of substance. In the table only calculated values L_v are given.

Some values were determined on molar coupling constants.

Pages 125-126.

PARAMETERS OF THE SOLUBILITY OF DIFFERENT ORGANIC COMPOUNDS.

Растворитель (1)	Формула (2)	Температура кипения, °C (3)	L_p (кал/моль) (расчет) (4)	σ_p (ккал/моль) ^{1/2} (5)	Данные (6)
Вода	H ₂ O	100	8875	21,2	Не растворяется (8)
Метанол (9)	CH ₃ OH	64,7	7764	13,4	То же
Этанол (11)	CH ₃ CH ₂ OH	78,5	7970	11,1	"
n-Пропанол (12)	CH ₃ CH ₂ CH ₂ OH	97,2	8830	10,4	"
n-Бутанол (13)	CH ₃ CH ₂ CH ₂ CH ₂ OH	117,7	9634	9,7	"
Этилкарбонат (14)	$\begin{array}{c} \text{C}_2\text{H}_5-\text{O} \\ \text{HO}-\text{C}=\text{O} \end{array}$	—	16860	14,9	"
Диэтилкарбонат (15)	$\begin{array}{c} \text{C}_2\text{H}_5-\text{O} \\ \text{C}_2\text{H}_5-\text{O}-\text{C}=\text{O} \end{array}$	126,3	8703	8,25	"
Диметилкарбонат (16)	$\begin{array}{c} \text{CH}_3-\text{O} \\ \text{CH}_3-\text{O}-\text{C}=\text{O} \end{array}$	90	8288	9,9	"
Этиленкарбонат (17)	$\begin{array}{c} \text{CH}_2-\text{O} \\ \\ \text{CH}_2-\text{O}-\text{C}=\text{O} \end{array}$	238	15250	12,7	(18) Растворяется при 70—80°
1,2-Пропиленкарбонат (19)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{O} \\ \\ \text{CH}_2-\text{O}-\text{C}=\text{O} \end{array}$	232,5	14230	11,9	Растворяется при 120—130°
2,3-Бутиленкарбонат (20)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{O} \\ \\ \text{CH}-\text{O}-\text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	243	14640	11,3	Растворяется при 180—190°
Диметилсульфон (21)	$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{S} \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$	238	12090	14,0	Растворяется при 105—110°
Метилэтилсульфон (22)	$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{S} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_5 \end{array}$	242,5	14871	13,9	Растворяется при 125—130°
Диэтилсульфон (23)	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{S} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_5 \end{array}$	248	14880	12,6	Растворяется при 160—170°
Метилпропилсульфон (24)	$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{S} \\ \diagdown \quad \diagup \\ \text{C}_3\text{H}_7 \end{array}$	257	15250	11,8	Растворяется при 170—180°

Key: (1). Solvent. (2). Formula. (3). Boiling point of °C. (4). kcal/mole (calculation). (5). (cal/cm³)^{1/2}. (6). Behavior of PAN. (7). Water. (8). It is not dissolved. (9). Methanol. (10). The same. (11). Ethanol. (12). n-Propanol. (13). n-Butanol. (14). Ethyl carbonate. (15). Diethylcarbonate. (16). Dimethylcarbonate. (17). Ethylene carbonate. (18). It is dissolved with. (19). 1,2-Propylene-carbonate. (20). 2,3-Butylenecarbonate. (21). Dimethylsulfone. (22). Methyl ethylsulfone. (23). Diethylsulfone. (24). Methylpropyl-sulfone.

Pages 127-128.

Continued.

Дипрапилсульфон		270,5	1820	10	Не растворяется
Тетраметилсульфон (3)		287	16604	14,0	Растворяется
3-Метилтетраметилсульфон (5)		279,5 (при 758 мм рт. ст.)	16226	12,5	Растворяется при 120
2,2-Диметилтетраметилсульфон (7)		287	16604	14	Растворяется
3,3'-Диметилтетраметилсульфон (8)		—	—	9,8	Не растворяется
Бис-(4-цианобутил)-сульфон (9)		—	—	11,8	Растворяется (10)
Этилен-1,2-бис-(этилсульфон) (11)		—	—	10,8	Сильно набухает (12)
2-Гидроксиэтилметилсульфон (13)		—	—	10,6	То же (14)
Диаллилсульфон (15)		109	8,960	9,5	Набухает (16)
Сульфонал (17)		300	17,200	9,1	Не растворяется (18)
Диметилсульфоксид (18)		189	13,650	13,6	Растворяется (19)
Диэтилсульфоксид (19)		89 (при 15 мм рт. ст.)	8,310	8,9	Набухает (20)

Key: (1). Dipropylsulfone. (2). It is not dissolved. (3). Tetramethylenesulfone. (4). It is dissolved with. (5). β -methyltetramethylenesulfone. (6). (with ... mm Hg). (7). $\alpha\alpha$ -Dimethyltetramethylenesulfone. (8). $\beta\beta$ -Dimethyltetramethylenesulfone. (9). Bis-(4-cyanobutyl)-sulfone. (10). It is dissolved. (11). Ethylene-1,2-bis-(ethylsulfone). (12). Strongly swells. (13). 2-Hydroxyethylmethylsulfone. (14). The same. (15). Diallylsulfone. (16). It will swell. (17). Sulfonal. (18). Dimethyl sulfoxide. (19). Diethylsulfoxide.

Pages 129-130.

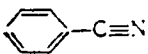
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Метил-н-бутилсульфоксид	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}(=\text{O})\text{CH}_3$	—	—	10,2	То же
Бис-(β-гидроксиэтил)-сульфоксид (3)	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{S}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{OH}$	157,7	11,200	9,11	Не растворяется
Тетраметиленсульфоксид (5)	$\text{CH}_2-\text{CH}_2-\text{S}(=\text{O})-\text{CH}_2-\text{CH}_2$	—	—	10,7	(4) Сильно набухает
Бис-(β-цианэтил)-сульфид (7)	$\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{N}\equiv\text{C}$	—	—	11,3	(3) Растворяется
Этиловый эфир (9)	$\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	34,6	6,247	6,8	Не растворяется
Бис-(β-цианэтил)-оксид (10)	$\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}\equiv\text{C}$	—	—	6,0	То же (2)
1,4-Диоксан (12)	$\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$	100	8,672	9,8	(4) Не растворяется
Диоксанон (13)	$\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}(=\text{O})-\text{O}$	—	—	11,6	(3) Растворяется
γ-Пирон (14)	$\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{O}$	216,5	13,505	12,7	(3) Растворяется при 125—150°
Ацетон (16)	$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$	56	5,900	5,6	Не растворяется
Метилэтилкетон (17)	$\text{CH}_3-\text{C}(=\text{O})-\text{C}_2\text{H}_5$	80	7,908	9,1	То же (2)
Циклобутанон (15)	$\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2$	99	8,670	10,5	•
Циклопентанон (19)	$\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2$	130	9,778	10,1	•
Циклогексанон (20)	$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2$	155	10,700	9,8	•
Ацетонитрил (21)	CH_3CN	82	7,982	11,9	Набухает (2)
Пропионитрил (23)	$\text{CH}_3\text{CH}_2\text{CN}$	98	8,603	10,8	•
Бутронитрил (24)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	117,4	9,350	10,2	Не растворяется
Капронитрил (25)	$\text{CH}_3(\text{CH}_2)_4\text{CN}$	102	11,140	9,4	То же (2)
Акрилонитрил (26)	$\text{CH}_2=\text{CHCN}$	77,3	7,835	12,3	•

Key: (1). Methyl--butylsulfoxide. (2). The same. (3).
Bis-(β -hydroxyethyl)-sulfoxide. (4). It is not dissolved. (5).
Tetramethylenesulfoxide. (6). Strongly it will swell. (7).
Bis-(β -cyanoethyl)-sulfide. (8). It is dissolved. (9). Ethyl
ether. (10). It is not dissolved. (11). Bis-(β -cyanoethyl)-oxide.
(12). 1,4-Dioxane. (13). Dioxane. (14). γ -pyrone. (15). It is
dissolved with. (16). Acetone. (17). Methyl ethyl ketone. (18).
Cyclobutanone. (19). Cyclopentanone. (20). Cyclohexanone. (21).
Acetonitrile. (22). It will swell. (23). Propionitrile. (24).
Butyronitrile. (25). Capronitrile. (26). Acrylonitrile.

Pages 131-132.

Continued.

Винилиденцианид (1)	$\text{CH}_2=\text{C}(\text{CN})_2$	153,5	—	14,4	•
Бензонитрил (2)		191	12,350	10,7	•
Малононитрил (3)	$\text{N}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{N}$	219	13,540	14,3	Сильно набухает
Метилмалононитрил (5)	$\text{N}\equiv\text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{C}\equiv\text{N}$	198	12,620	11,5	Не растворяется
Диметилмалононитрил (7)	$\text{N}\equiv\text{C}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{C}\equiv\text{N}$	169,5	11,470	11,4	То же (8)
Пропилмалононитрил (9)	$\text{N}\equiv\text{C}-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{C}\equiv\text{N}$	210	13,090	10,3	•
Сукцинонитрил (10)	$\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$	266	15,660	13,6	Растворяется при 145°
Метилсукцинонитрил (12)	$\text{CH}_3-\underset{\text{CH}_2-\text{CN}}{\text{CH}}-\text{CN}$	253	15,050	13,0	Не растворяется
1,2-Диметилсукцинонитрил (13)	$\text{CH}_3-\underset{\text{CH}_3-\text{CH}-\text{CN}}{\text{CH}}-\text{CN}$	219	13,550	11,5	То же (8)
Глутаронитрил (14)	$\text{CH}_2-\underset{\text{CH}_2-\text{CN}}{\text{CH}}-\text{CH}_2-\text{CN}$	287	16,584	13,0	Растворяется при 145°
Адипонитрил (15)	$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$	295	16,963	13,2	Растворяется при 145°
Фумаронитрил (16)	$\text{NC}-\underset{\text{CH}=\text{CN}}{\text{CH}}-\text{CN}$	186	10,044	10,9	Сильно набухает
Гидроксиацетонитрил (17)	HOCH_2CN	183	12,010	14,8	То же (8)
β-Гидроксипропионитрил (18)	$\text{HOCH}_2\text{CH}_2\text{CN}$	220	13,600	13,9	Растворяется
Хлорацетонитрил (20)	ClCH_2CN	124	9,625	12,4	•
Гексаметилендицианид (21)	$\text{NC}(\text{CH}_2)_6\text{CN}$	185	10,020	8,5	Не растворяется
9-Метоксипропионитрил (22)	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CN}$	165,5	11,290	10,9	То же (8)
α-Гидроксипропионитрил (23)	$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CN}$	182	12,080	12,9	Набухает
α-Гидроксизобутиро- нитрил (25)	$\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CN}$	82	7,970	9,0	Не растворяется
1,3,2,5-Тетрацианспентан (26)	$\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\underset{\text{CN}}{\overset{\text{CN}}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$	—	—	9,3	Набухает (24)

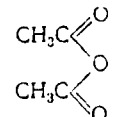
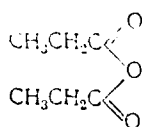
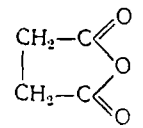
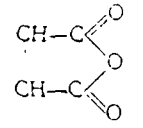
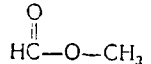
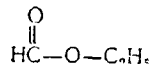
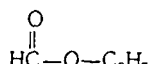
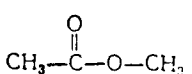
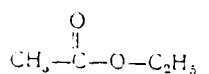
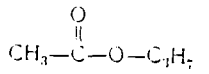
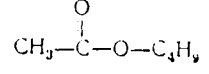
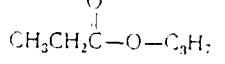
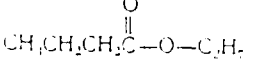
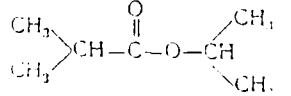
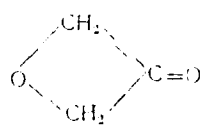
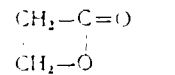
(21a) (при 15 мм рт. ст.)

(21b) (при 23 мм рт. ст.)

Key: (1). Vinylidenecyanide. (2). Benzonitrile. (3). Malononitrile. (4). Strongly it will swell. (5). Methylmalononitrile. (6). It is not dissolved. (7). Dimethylmalononitrile. (8). The same. (9). Propylmalononitrile. (10). Succinonitrile. (11). It is dissolved at. (12). Methylsuccinonitrile. (13). 1,2-Dimethylsuccinonitrile. (14). Glutaronitrile. (15). Adiponitrile. (16). Fumaronitrile. (17). Hydroxyacetonitrile. (18). β -Hydroxypropionitrile. (19). It is dissolved. (20). Chloroacetonitrile. (21). Hexamethylenedicyanide. (21a). (with ... mm Hg). (22). β -Methoxypropionitrile. (23). α -Hydroxypropionitrile. (24). It will swell. (25). α -Hydroxyisobutyronitrile. (26). 1,3,3,5-Tetracyanopentane.

Pages 133-134.

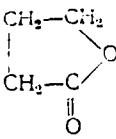
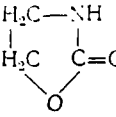
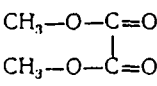
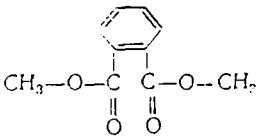
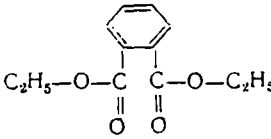
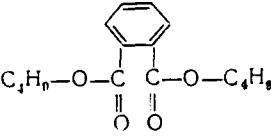
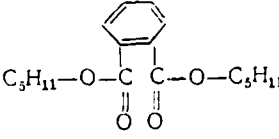
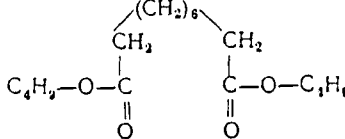

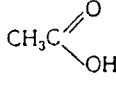
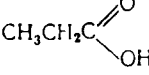
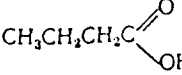
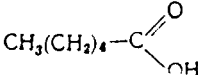
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Уксусный ангидрид		140	10,249	10,6	Не растворяется
Пропионовый ангидрид (3)		165	11,257	9,7	То же (4)
Янтарный ангидрид (5)		261	15,409	13,5	Растворяется при 120—125°
Малеиновый ангидрид (7)		193	12,610	10,7	Растворяется при 135—140°
Метилформиат (8)		32	5,781	10,4	Не растворяется
Этилформиат (9)		54,3	6,949	10,1	То же (4)
Пропилформиат (10)		81,3	7,593	9,1	"
Метилацетат (11)		57,5	7,539	9,7	"
Этилацетат (12)		76,1	7,759	9,1	Не растворяется
Пропилацетат (13)		101,8	8,741	8,9	То же (4)
Бутилацетат (14)		124	9,613	7,1	"
Пропилпропионат (15)		122,4	9,548	8,6	"
Пропилбутират (16)		142,7	10,358	8,5	"
Изопропилизобутират (17)		120,5	9,473	8,1	"
Метиленгликолят (18)		150	10,872	11,7	Растворяется при 120°
Пиролактон (19)		160	11,052	12,7	Растворяется при 100°

Key: (1). Acetic anhydride. (2). It is not dissolved. (3). Propionic anhydride. (4). The same. (5). Succinic anhydride. (6). It is dissolved at. (7). Maleic anhydride. (8). Methylformate. (9). Ethylformate. (10). Propyl-formate. (11). Methyl acetate. (12). Ethylacetate. (13). Propylacetate. (14). Butyl acetate. (15). Propyl-propionate. (16). Propyl-butyrate. (17). Isopropylisobutyrate. (18). Methylene glycolate. (19). Propiolactone.

Pages 135-136.

Continued.

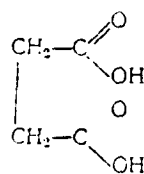
Бутиролактон		204	11,905	14,5	Растворяется при 120°
2-Оксазолидон (3)		—	—	10,1	Сильно набухает
Диметилноксалат (5)		163,3	11,080	10,4	Не растворяется
Диметилфталат (7)		283,7	—	8,8	То же (6)
Диэтилфталат (9)		194	—	8,9	"
Дибутилфталат (10)		338	—	9,1	"
Диамилфталат (11)		344	—	9,2	Не растворяется
Дибутилсебацнат (12)		345	—	8,5	То же (8)
Муравьиная кислота (13)		100,5	8,692	12,6	Сильно набухает
Уксусная кислота (14)		118,5	9,394	11,5	Набухает (15)
Пропионовая кислота (16)		141,1	10,274	10,9	Не растворяется
Масляная кислота (17)		163,0	11,185	10,4	То же (8)
Капроновая кислота (18)		205,3	12,951	9,8	"

Key: (1). Butyrolactone. (2). It is dissolved at. (3).
2-Oxazoleide. (4). Strongly it will swell. (5). Dimethyloxalate.
(6). It is not dissolved. (7). Dimethyl phthalate. (8). The same.
(9). Diethyl phthalate. (10). Dibutyl phthalate. (11).
Diamylphthalate. (12). Dibutylsebacate. (13). Formic acid. (14).
Acetic acid. (15). It will swell. (16). Propionic acid. (17).
Butyric acid. (18). Caproic acid.

Pages 137-138.

Continued.

Ятарная кислота



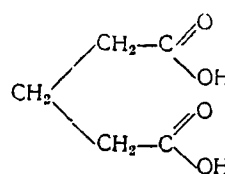
235

14,251

10,2

Глутаровая кислота

(2)

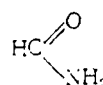


235

17,337

10,6

Формамид (3)

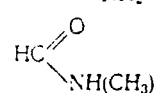


23

12,450

17,5

N-Метилформамид (4)



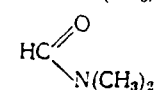
23

11,723

11,7

Набухает (5)

N,N-Диметилформамид (6)



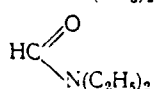
23

10,776

12,1

Растворяется при 20°

N,N-Диэтилформамид (8)



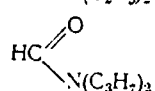
23

11,848

10,7

Не растворяется

N,N-Дипропилформамид (10)



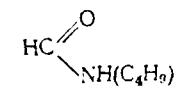
—

—

9,0

То же (11)

N-Бутилформамид (12)



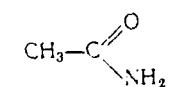
—

7,970

8,1

Не растворяется

Ацетамид (13)



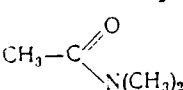
222

13,682

11,6

То же (11)

N,N-Диметилацетамид (14)



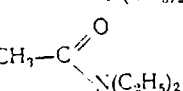
165,3

11,266

11,7

Растворяется при 15°

N,N-Диэтилацетамид (16)



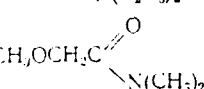
165,5

12,100

10,0

Не растворяется

Диметилметоксиацетамид (17)



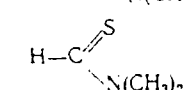
—

—

12,1

Растворяется (15)

Диметилтиоформамид (19)

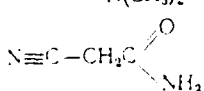


—

—

13,6

Цианацетамид (20)



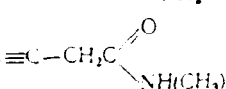
11,0

8452

10,0

Растворяется при 165—170°

N-Метилцианонацетамид (21)



—

—

13,4

Растворяется при 180—190°

Key: (1). Succinic acid. (2). Glutaric acid. (3). Formamide.
(4). N-Methylformamide. (5). It will swell. (6).
N,N-Dimethylformamide. (7). It is dissolved at. (8).
N,N-Diethylformamide. (9). It is not dissolved. (10).
N,N-Dipropyl-formamide. (11). The same. (12). N-Butylformamide.
(13). Acetamide. (14). N,N-Dimethylacetamide. (15). It is
dissolved with. (16). N,N-Diethylacetamide. (17).
Dimethylmethoxyacetamide. (18). It is dissolved. (19).
Dimethylthioformamide. (20). Cyanacetamide. (21).
N-Methylcyanoacetamide.

Pages 139-140.

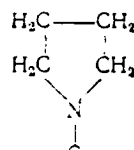
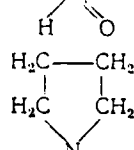
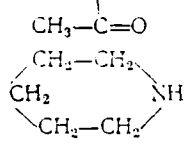
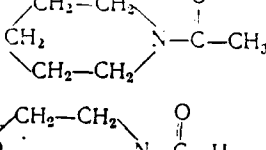
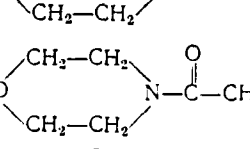
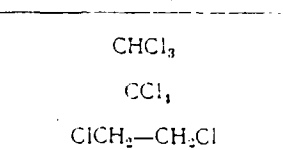

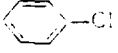
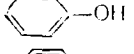
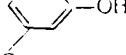
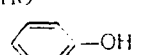
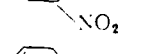
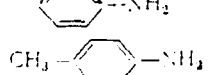
Continued.

N,N-Диметилацетамид	<chem>CN(C)C(=O)C#N</chem>	—	—	14,5	Растворяется при 150—160°
Диметилксамид (3)	<chem>CN(C)C(=O)C(=O)N(C)C</chem>	—	9,130	9,8	Не растворяется
Тетраметилмочевина (5)	<chem>CN(C)C(=O)N(C)C(=O)N(C)C</chem>	177,5	11,780	9,7	То же (4)
N-Метилдиацетамид (7)	<chem>CN(C)C(=O)C(=O)N(C)C</chem>				"
Метоксиацетамид (8)	<chem>CN(C)C(=O)CO</chem>	192	12,380	12,2	"
Этиленмочевина (9)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	—	8,460	10,2	"
1,6-Гексаметилендиамин (10)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	204	12,900	9,3	"
Дикетопиперазин (11)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	260	15,360	21,2	"
α-Пирролидон (12)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	245	14,595	13,5	Растворяется при 130—140°
α-Пиперидон (13)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	255	15,194	12,7	Растворяется при 100°
ε-Капролактam (14)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	260	15,300	12,1	Растворяется при 100°
N,N-Диформилпиперазин (15)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	337,4	18,959	12,0	Растворяется при 125°
N,N-Диацетилпиперазин (16)	<chem>CN(C)C(=O)NCCNC(=O)N</chem>	370	20,657	11,5	Сильно набухает

Key: (1). N,N-Dimethylcyanoacetamide. (2). It is dissolved with.
(3). Dimethyloxamide. (4). It is not dissolved. (5).
Tetramethylurea. (6). The same. (7). N-Methyldiacetamide. (8).
Methoxyacetamide. (9). Ethylene-urea. (10).
1.6-Hexamethylenediamine. (11). Diketopiperazine. (12).
 α -Pyrrolidone. (13). α -Piperidone. (14). ϵ -Caprolactam. (15).
N,N-Diformylpiperazine. (16). N,N-Diacetylpiperazine. (17).
Strongly it will swell.

Pages 141-142.

Continued.

N-Формилпирролидин (1)		219	13,680	12,1	Растворяется
N-Ацетилпирролидин (3)		220	13,954	11,5	Растворяется при 100°
Н-Пиперидин (5)		190	8,944	9,1	Набухает
N-Ацетилпиперидин (7)		227	13,900	10,3	Сильно набухает
N-Формилморфолин (9)		222	13,680	10,6	Растворяется при 83—95°
N-Ацетилморфолин (10)		239	14,472	10,4	Растворяется при 150°
Метиленхлорид (11)	CH ₂ Cl ₂	40,1	6,750	10,4	Не растворяется
Хлорформ (13)	CHCl ₃	61,5	7,280	9,1	Не растворяется
Четыреххлористый углерод (13a)	CCl ₄	76	7,870	8,3	То же (14)
1,2-Дихлорэтан (14a)	ClCH ₂ —CH ₂ Cl	83,6	8,250	10,7	"
Бромистый этил (15)	CH ₃ CH ₂ Br	88,4	6,507	9,1	"
Бромистый пропил (16)	CH ₃ CH ₂ CH ₂ Br	100,9	7,670	9,2	"
Тетрахлорэтан (17)	Cl ₂ CH—CHCl ₂	146,2	10,499	9,3	"
Бензол (18)		80,1	6,576	7,8	"
Хлорбензол (19)		132	10,315	9,6	"
Фенол (20)		182,1	11,978	11,1	"
m-Крезол (21)		202,2	12,829	10,6	"
p-Крезол (22)		216	13,419	12,4	"
Анилин (23)		184,4	12,075	11,2	Набухает (6)
n-Толуидин (24)		200,5	12,756	10,3	Не растворяется

Key: (1). N-Formylpyrrolidine. (2). It is dissolved. (3). N-Acetylpyrrolidine. (4). It is dissolved at. (5). α -Piperidine. (6). It will swell. (7). N-Acetylpiperidine. (8). Strongly it will swell. (9). N-Formylmorpholine. (10). N-Acetylmorpholine. (11). Methylene chloride. (12). It is not dissolved. (13). Chloroform. (13a). Carbon tetrachloride. (14). The same. (14a). 1,2-Dichloroethane. (15). Ethyl bromide. (16). Bromide propyl. (17). Tetrachloroethane. (18). Benzene. (19). Chlorobenzene. (20). Phenol. (21). m-Cresol. (22). o-Nitrophenol. (23). Aniline. (24). p-Toluidine.

Pages 143-144.

Соединения

Диметиланилин (3)		194.1	12.484	9.7	То же (1)
Нитробензол (3)		210.9	13.202	10.9	"
Метилтиоцианат (4)	$\text{CH}_3-\text{S}-\text{C}\equiv\text{N}$	119	9.440	9.0	"
1,6-Гексаметилендитиоцианат (5)	$\text{N}\equiv\text{C}-\text{S}-(\text{CH}_2)_6-\text{S}-\text{C}\equiv\text{N}$	—	—	11.4	"
Трис-(диметилами́до)-фосфат (6)		—	—	11.2	(7) Растворяется при 150°
Тетра-(диметилами́до)-пи-рофосфат (8)		—	—	10.9	(8) Растворяется при 150°
Диметилфосфат (9)	$(\text{CH}_3\text{O})_2\text{P}=\text{O}$ OH	167	—	6.2	(10) Не растворяется
Диметилэтилфосфат (11)		148	—	7.2	То же (2)
Хлоральгидрат (12)		—	—	4.7	Не растворяется
Нитрометан (13)	CH_3NO_2	101	8.672	12.2	Растворяется (1)
Нитроэтан (15)	$\text{CH}_3\text{CH}_2\text{NO}_2$	114.8	9.256	11.0	Не растворяется
Нитропропан (16)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	132	10.328	10.4	То же (2)
N,N-Диметилнитрамин (17)		187	12.184	12.0	Растворяется при 140—160°
Окись пропилена (18)		35.0	6.248	9.9	Не растворяется
Тетрагидрофуран (19)		64.5	7.409	9.7	То же (2)
Тетрагидропиран (20)		88	8.212	9.1	"

Key: (1). Dimethylaniline. (2). The same. (3). Nitrobenzene.
(4). Methylthiocyanate. (5). 1,6-Hexamethylenedithiocyanate. (6).
Tris-(dimethylamido)-phosphate. (7). It is dissolved at. (8).
Tetra-(dimethylamido)-pyrophosphate. (9). Dimethyl phosphate. (10).
It is not dissolved. (11). Dimethylethylphosphate. (12).
Chloralhydrate. (13). Nitromethane. (14). It is dissolved. (15).
Nitroethane. (16). Nitropropane. (17). N,N-Dimethylnitramine.
(18). Propylene oxide. (19). Tetrahydrofuran. (20).
Tetrahydropyran.

Pages 145-146.

Appendix III.

PROPERTIES OF DIFFERENT FIBERS FROM POLYMERS AND COPOLYMERS OF ACRYLONITRILE.

Страна и завод- производи- тель, или город	2. Волокно	3. Тип волокна	4. Химический состав волокна	5. Способ прядения	6. Удель- ный вес г/см ³	7. Темпера- тура размягче- ния °C	8. Прочность разр. кМ		9. Удлинение %		10. Относи- тельная проч- ность в петле %	11. Натяж- ный модуль кг/мм ²	12. Сред- няя плот- ность г/см ³
							а) сухого	б) мок- рого	а) сухого	б) мок- рого			
СССР	Нитрон (15)	(16) Штапель	Полиакрилонитрил (18)	(19) Мокрый: вод- ный	1,15	225—245	22—29	20—21	23—32	23—32	40—50	480	78
		(17) Шелк		(20) Мокрый: ор- ганические ванны	1,15	225—245	43—55	44—52	14—17	14—17	—	—	—
США Du Pont	(21) Орлон	(16) Штапель	(22) Сополимер акрило- нитрила с эфира- ми акриловой кис- лоты	Сухой (23)	1,14	138—150	14—20	13—15	25—34	25—34	60—70	150	75
		(17) Шелк			1,14	235	30—40	—	14—15	—	—	825	—
Chemst- gard	Акрилан (24)	Штапель (16)	(25) Сополимер акрило- нитрила с винил- ацетатом и винил- пиридином	Мокрый: вод- ный (19)	1,173	240	20—25	16—20	35—38	35—38	50—70	394	67
	Дарлан (26)	Штапель (16)	(27) Сополимер винил- идеинамида с ви- нил-ацетатом	Неизвестно (28)	1,18	170—175	15—18	13—14	25—35	25—35	—	95	—
					—	—	—	—	—	—	—	—	—
Акрилан, Креслан (Ludacril (N-51))	(29)	Штапель (16)	(30) Сополимер акрило- нитрила с акрил- амидом	Мокрый: вод- ный (31) Неизвестно (32)	1,17	190	20—22	—	30—35	—	—	—	—
					—	—	30—35	—	18—22	—	—	—	—
Dom. Che- mical	Зефран (33)	Штапель (16)	(34) Привитый или блок- сополимер акри- лонитрила с ви- нил-ацетатом и ви- нилпирролидином	Мокрый: вод- ный (19)	1,19	255	30—32	27—28	30—35	30—35	—	—	—
Воль- крон	(34)	(16)	(35) Полиакрилонитрил	Мокрый: вод- ный (19)	1,16	220—235	18—23	17—22	18—25	18—25	40—45	410	—
Акри- лан	Пирелан (36)	(16)	(35) Полиакрилонитрил	Мокрый: ор- ганические ванны (35)	1,17	230—245	25—35	24—34	30—40	30—40	50—60	400	—
А. Вауер	Дракон (37)	(16)	(40) Сополимер акрило- нитрила с эфира- ми акриловой кис- лоты	Сухой (23)	1,15	—	22—25	—	30—35	—	—	—	—

Key: (1). Country and manufacturer or city. (2). Fiber. (3). Type of fiber. (4). Chemical composition of fiber. (5). Method of spinning. (6). Specific weight g/cm³. (7). Softening temperature of °C. (8). Strength, breaking km. (9). dry. (10). wet. (11). Elongation. (12). Relative loop strength %. (13). Initial modulus kgf/mm². (14). Elasticity of fiber %. (15). Nitron. (16). Staple. (17). Silk. (18). Polyacrylonitrile. (19). Wet; water/aqueous. (20). Wet; organic baths. (21). Orlon. (22). Copolymer of acrylonitrile with acrylic esters. (23). Dry. (24). Acrilan. (25). Copolymer of acrylonitrile with vinyl acetate and vinylpyridine. (26). Darlan. (27). Copolymer of vinylidenecyanide with vinyl acetate. (28). It is unknown. (29). Creslan. (30). Copolymer of acrylonitrile with acrylamide. (31). Zefran. (32). They are grafted or block copolymer of acrylonitrile with vinyl acetate and vinylpyrrolidone. (33). GDR city of Wolfen. (34). Wolkrilon. (35). Polyacrylonitrile. (36). city of Premnitz. (37). Prelan. (38). Wet; organic baths. (38a). FRG A. Bauyer. (39). Dralon. (40). Copolymer of acrylonitrile with acrylic esters. (41). Dry.

Page 147.

Continued.

11	2 m.	Пан	Штапель	Полиакрилонитрил	Мокрый: вод- ный	1,16	235	17—25	14—22	20—35	20—35	30—40	—	—
		(5)	(6)	(7)	(8)	1,14	115—125	33—45	—	18—22	—	—	—	—
12	Г. Gesell- schaff Co	Редон	Шелк	Сополимер	Сухой	(9)	—	—	25—30	22—27	30—40	30—40	—	—
	(10)	(9)	(6)	(7)	(8)	—	—	—	25—30	22—27	30—40	30—40	—	—
13	Англия	(11)	(12)	(13)	(14)	1,15	>200	29—34	22—26	40—45	40—45	—	—	—
	Санта- Круа	Куртель	Штапель	Сополимер акрило- нитрила с эфир- ми акриловый нит- раты	Мокрый: вод- ный	(15)	—	—	—	—	—	—	—	—
	(16)	(11)	(12)	(13)	(14)	1,12	165	20—30	—	20—30	—	—	—	—
14	Франция	(17)	(18)	(19)	(20)	—	—	18—22	—	До 40	—	50—90	—	—
	Крило- Р	Крило- Р	Штапель	Сополимер акрило- нитрила с метил- метакрилатом	Мокрый	(21)	—	—	—	—	—	—	—	—
	(17)	(18)	(19)	(20)	(21)	—	—	—	—	—	—	—	—	—
15	Шве- ция	(22)	(23)	(24)	(25)	—	—	—	—	—	—	—	—	—
	Супер- про- риал Co	Такрил	Штапель	Полиакрилонитрил	Мокрый: ор- ганические ванны	(26)	—	—	—	—	—	—	—	—
	(21)	(22)	(23)	(24)	(25)	—	—	—	—	—	—	—	—	—
16	Бель- гия	(27)	(28)	(29)	(30)	—	—	—	—	—	—	—	—	—
	Акри- бель	Акри- бель	Штапель	Сополимер акрило- нитрила с метил- метакрилатом	Мокрый: вод- ный	(31)	—	—	25	22	27	27	—	—
	(21)	(22)	(23)	(24)	(25)	—	—	—	—	—	—	—	—	—

Key: (1). Pan-. (2). Staple. (3). Polyacrylonitrile. (4). Wet; water/aqueous. (5). Dolan. (6). Silk. (7). Copolymer. (8). Dry. (9). Redon. (10). England. (11). Courtelle. (12). Copolymer of acrylonitrile with acrylic esters. (13). France. (14). Krilor. (15). Copolymer of acrylonitrile with methylemethacrylate. (16). Wet. (17). Sweden. (18). Takril. (19). Polyacrylonitrile. (20). Wet; organic baths. (21). Belgium. (22). Akribel. (23). Copolymer of acrylonitrile with methylemethacrylate.

Page 148. NO TYPING.

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